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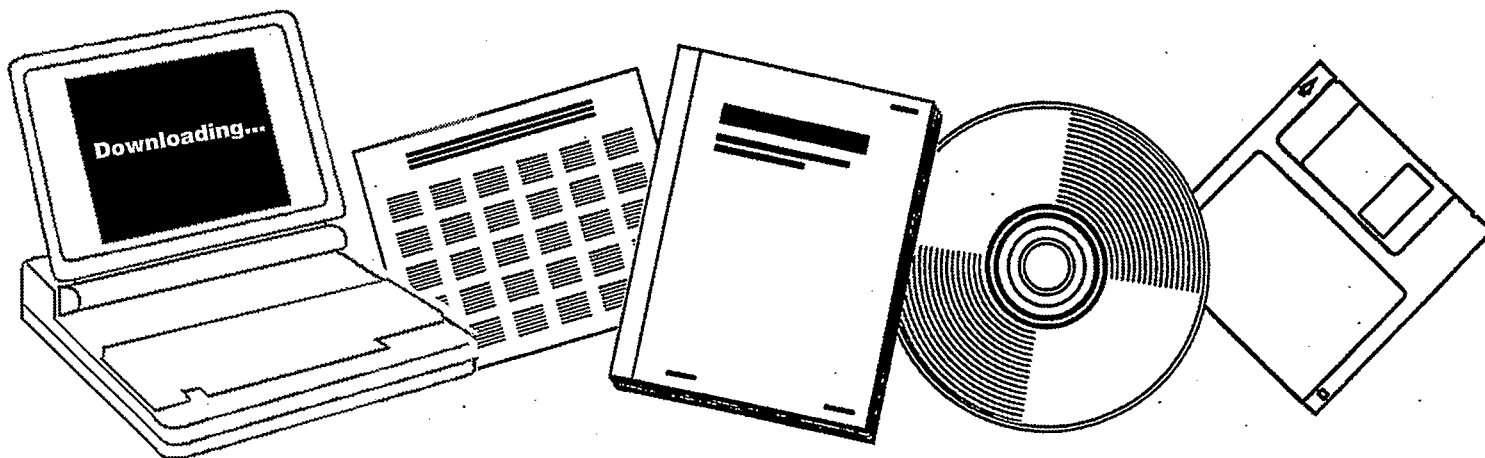
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**CHEMISTRY AND CATALYSIS OF COAL  
LIQUEFACTION CATALYTIC AND THERMAL  
UPGRADING OF COAL LIQUID AND HYDROGENATION  
OF CO TO PRODUCE FUELS. QUARTERLY PROGRESS  
REPORT, JANUARY-MARCH 1981**

UTAH UNIV., SALT LAKE CITY. DEPT. OF  
MINING AND FUELS ENGINEERING

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Chemistry and Catalysis of Coal Liquefaction  
Catalytic and Thermal Upgrading of Coal Liquid  
and Hydrogenation of CO to Produce Fuels

Quarterly Progress Report  
for the Period Jan - Mar 1981

Dr. Wendell H. Wiser

University of Utah - Department of  
Mining and Fuels Engineering  
Salt Lake City, Utah 84112

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## OBJECTIVE AND SCOPE OF WORK

### I. The chemistry and Catalysis of Coal Liquefaction

#### Task 1 Chemical-Catalytic Studies

Coal will be reacted at subsoftening temperatures with selective reagents to break bridging linkages between clusters with minimal effect on residual organic clusters. The coal will be pretreated to increase surface area and then reacted at 25 to 350°C. Reagents and catalysts will be used which are selective so that the coal clusters are solubilized with as little further reaction as possible.

#### Task 2 Carbon-13 NMR Investigation of CDL and Coal

Carbon-13 NMR spectroscopy will be used to examine coal, coal derived liquids (CDL) and residues which have undergone subsoftening reactions in Task 1 and extraction. Improvements in NMR techniques, such as crosspolarization and magic angle spinning, will be applied. Model compounds will be included which are representative of structural units thought to be present in coal. Comparisons of spectra from native coals, CDL and residues will provide evidence for bondings which are broken by mild conditions.

#### Task 3 Catalysis and Mechanism of Coal Liquefaction

This fundamental study will gain an understanding of metal salt chemistry and catalysis in coal liquefaction through study of reactions known in organic chemistry. Zinc chloride and other catalytic materials will be tested as Friedel-Crafts catalysts and as redox catalysts using coals and selected model compounds. Zinc chloride, a weak Friedel-Crafts catalyst, will be used at conditions common to coal liquefaction to participate in well defined hydrogen transfer reactions. These experiments will be augmented by mechanistic studies of coal hydrogenation using high pressure thermogravimetric analysis and structural analysis. The results of these studies will be used to develop concepts of catalysis involved in coal liquefaction.

#### Task 4 Momentum Heat and Mass Transfer in CoCurrent Flow of Particle-Gas Systems for Coal Hydrogenation

A continuation of ongoing studies of heat and transport phenomena in cocurrent, co-gravity flow is planned for a one-year period. As time and development of existing work permits, the extension of this study to include a coiled reactor model will be undertaken. Mathematical models of coal hydrogenation systems will utilize correlations from these straight and coiled reactor configurations.

#### Task 5 The Fundamental Chemistry and Mechanism of Pyrolysis of Bituminous Coal

Previous work at the University of Utah indicates that coal pyrolysis, dissolution (in H-donor) and catalytic hydrogenation all have similar rates and activation energies. A few model compounds will be pyrolyzed in the range of 375 to 475°C. Activation energies, entropies and pro-

duct distributions will be determined. The reactions will assist in formulating the thermal reaction routes which also can occur during hydro-liquefaction.

## II. Catalytic and Thermal Upgrading of Coal Liquids

### Task 6 Catalytic Hydrogenation of CD Liquids and Related Polycyclic Aromatic Hydrocarbons

A variety of coal derived (CD) liquids will be hydrogenated with sulfided catalysts prepared in Task 10 from large pore, commercially available supports. The hydrogenation of these liquids will be systematically investigated as a function of catalyst structure and operating conditions. The effect of extent of hydrogenation will be the subject of study in subsequent tasks in which crackability and hydrolysis of the hydrogenated product will be determined. To provide an understanding of the chemistry involved, model polycyclic arenes will be utilized in hydrogenation studies. These studies and related model studies in Task 7 will be utilized to elucidate relationships between organic reactants and the structural-topographic characteristics of hydrogenation catalysts used in this work.

### Task 7 Denitrogenation and Deoxygenation of CD Liquids and Related Nitrogen- and Oxygen-Containing Compounds

Removal of nitrogen and oxygen heteroatoms from CD liquids is an important upgrading step which must be accomplished to obtain fuels corresponding to those from petroleum sources. Using CD liquids as described in Task 6, exhaustive HDN and HDO will be sought through study of catalyst systems and operating conditions. As in Task 6, catalysts will be prepared in Task 10 and specificity for N- and O-removal will be optimized for the catalyst systems investigated. Model compounds will also be systematically hydrogenated using effective HDN/HDO catalysts. Kinetics and reaction pathways will be determined. A nonreductive denitrogenation system will be investigated using materials which undergo reversible nitridation. Conditions will be sought to cause minimal hydrogen consumption and little reaction of other reducible groups.

### Task 8 Catalytic Cracking of Hydrogenated CD Liquids and Related Polycyclic Naphthenes and Naphthenoaromatics

Catalytic cracking of hydrogenated CD liquid feedstocks will be studied to evaluate this scheme as a means of upgrading CD liquids. Cracking kinetics and product distribution as a function of preceding hydrogenation will be evaluated to define upgrading combinations which require the minimal level of CD liquid aromatic saturation to achieve substantial heteroatom removal and high yields of cracked liquid products. Cracking catalysts to be considered for use in this task shall include conventional zeolite-containing catalysts and large-pore molecular sieve, CLS (cross-linked smectites) types under study at the University of Utah. Model compounds will be subjected to tests to develop a mechanistic understanding of the reactions of hydro CD liquids under catalytic cracking conditions.

### Task 9 Hydropyrolysis (Thermal Hydrocracking) of CD Liquids

Heavy petroleum fractions can be thermally hydrocracked over a specific range of conditions to produce light liquid products without excessive hydrogenation occurring. This noncatalytic method will be applied to a variety of CD liquids and model compounds, as mentioned in Task 6, to determine the conditions necessary and the reactivity of these CD feedstocks with and without prior hydrogenation and to derive mechanism and reaction pathway information needed to gain an understanding of the hydropyrolysis reactions. Kinetics, coking tendencies and product compositions will be studied as a function of operating conditions.

### Task 10 Systematic Structural-Activity Study of Supported Sulfide Catalysts for Coal Liquids Upgrading

This task will undertake catalyst preparation, characterization and measurement of activity and selectivity. The work proposed is a fundamental study of the relationship between the surface-structural properties of supported sulfide catalysts and their catalytic activities for various reactions desired. Catalysts will be prepared from commercially available supports composed of alumina, silica-alumina, silica-magnesia and silica-titania, modification of these supports to change acidity and to promote interaction with active catalytic components is planned. The active constituents will be selected from those which are effective in a sulfided state, including but not restricted to Mo, W, Ni and Co. The catalysts will be pre-sulfided before testing. Catalyst characterization will consist of physico-chemical property measurements and surface property measurements. Activity and selectivity tests will also be conducted using model compounds singly and in combination.

### Task 11 Basic Study of the Effects of Coke and Poisons on the Activity of Upgrading Catalysts

This task will begin in the second year of the contract after suitable catalysts have been identified from Tasks 6, 7 and/or 10. Two commercial catalysts or one commercial catalyst and one catalyst prepared in Task 10 will be selected for a two-part study, (1) simulated laboratory poisoning/coking and (2) testing of realistically aged catalysts. Kinetics of hydrogenation, hydrodesulfurization, hydrodenitrogenation and hydrocracking will be determined before and after one or more stages of simulated coking. Selected model compounds will be used to measure detailed kinetics of the above reactions and to determine quantitatively how kinetic parameters change with the extent and type of poisoning/coking simulated. Realistically aged catalysts will be obtained from coal liquids upgrading experiments from other tasks in this program or from other laboratories conducting long-term upgrading studies. Deactivation will be assessed based on specific kinetics determined and selective poisoning studies will be made to determine characteristics of active sites remaining.

### Task 12 Diffusion of Polyaromatic Compounds in Amorphous Catalyst Supports

If diffusion of a reactant species to the active sites of the catalyst is slow in comparison to the intrinsic rate of the surface reaction, then only sites near the exterior of the catalyst particles will be utilized effectively. A systematic study of the effect of molecular size on the sorptive diffusion kinetics relative to pore geometry will

be made using specific, large diameter aromatic molecules. Diffusion studies with narrow boiling range fractions of representative coal liquid will also be included. Experimental parameters for diffusion kinetic runs shall include aromatic diffusion model compounds, solvent effects, catalyst sorption properties, temperature and pressure.

### III. Hydrogenation of CO to Produce Fuels

#### Task 13 Catalyst Research and Development

Studies with iron catalysts will concentrate on promoters, the use of supports and the effects of carbiding and nitriding. Promising promoters fall into two classes: (1) nonreducible metal oxides, such as CaO, K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and MgO, and (2) partially reducible metal oxides which can be classified as co-catalysts, such as oxides of Mn, Mo, Ce, La, V, Re and rare earths. Possible catalyst supports include zeolites, alumina, silica, magnesia and high area carbons. Methods of producing active supported iron catalysts for CO hydrogenation will be investigated, such as development of shape selective catalysts which can provide control of product distribution. In view of the importance of temperature, alternative reactor systems (to fixed bed) will be investigated to attain better temperature control. Conditions will be used which give predominately lower molecular weight liquids and gaseous products.

#### Task 14 Characterization of Catalysts and Mechanistic Studies

Catalysts which show large differences in selectivity in Task 13 will be characterized as to surface and bulk properties. Differences in properties may provide the key to understanding why one catalyst is superior to another and identify critical properties, essential in selective catalysts. Factors relating to the surface mechanism of CO hydrogenation will also be investigated. Experiments are proposed to determine which catalysts form "surface" (reactive) carbon and the ability of these catalysts to exchange C and O of isotopically labelled CO. Reactions of CO and H<sub>2</sub> at temperatures below that required for CO dissociation are of particular interest.

#### Task 15 Completion of Previously Funded Studies and Exploratory Investigations

This task is included to provide for the orderly completion of coal liquefaction research underway in the expiring University of Utah contract, EX-76-C-01-2006.

## Chemical-Catalytic Studies of Coal Liquefaction

Faculty Advisor: J. Shabtai  
Graduate Student: R. Jensen

### Introduction

This project is concerned with the development of suitable processing conditions and catalyst-solvent systems for coal liquefaction under mild temperature (<350°C) and pressure (<2000 psi).

### Present Status

One of the main conditions for effective use of catalyst-solvent systems in liquefaction below the coal softening point is the necessity of increasing the micropore volume of the solid coal. Previous studies in this Department show that pretreatment of coal with metal halides, e.g.  $ZnCl_2$ , at relatively mild temperatures (200-350°C) causes considerable increase in surface area and microporosity. Elucidation of the nature of chemical reactions between metal halides and coal has attracted recently considerable interest. In the framework of our work on preparation of highly porous coal feeds for subsequent use in homogeneously catalyzed liquefaction, it was considered of importance to develop a better understanding of such reactions. Therefore, systematic studies of metal halide-catalyzed reactions were undertaken, using the following types of model compounds:

- (a) Alkylbenzenes with branched alkyl groups;
- (b) Alkylbenzenes with n-alkyl groups; and
- (c) Diarylalkanes.

These studies were intended to provide information on

(1) the mode of catalytic activity of metal halides in a wide range of experimental conditions; and

(2) the direction and rate of metal halide-catalyzed dealkylation and hydrodealkylation processes, as related to cleavage reactions of inter-cluster linkages in the coal structure.

The present report provides partial results obtained in a study with model compounds of type (a) indicated above.

The dealkylation reactions of representative monoalkylbenzenes having branched alkyl substituents, i.e. isopropylbenzene, sec-butylbenzene, and tert-butylbenzene, in the presence of a silica gel-supported  $ZnCl_2$  catalyst, were systematically investigated in the 250-500°C temperature range.

Experiments were carried out both under hydrogen and under nitrogen pressure. The latter was kept constant at 850 psig for the purpose of comparison. Reactions were performed in a microreactor with an internal volume of 1 ml (to be described in a subsequent report). The reactor was of the batch type, with temperature monitored by a thermocouple connected to a calibrated chart recorder. The total reaction time in each run was



kept constant at 90 seconds. Products obtained were identified and quantitatively analyzed by a combination of gas chromatography and mass spectrometry.

Table 1 and Figures 1a and 1b summarize the change in product composition from the  $ZnCl_2$ -catalyzed hydrodealkylation of tert-butylbenzene (1) as a function of reaction temperature (250-500°C), keeping a constant reaction time of 90 seconds and a hydrogen pressure of 850 psig. Blank experiments in the absence of catalyst were carried out (Table 1a, last two columns).

As seen from Table 1 and Figure 1a, the conversion of 1 increases gradually with increase in temperature (from 4.4 to 68.6%). Further, it is observed that the main liquid product formed is benzene. The yield of this product is 94-95% at 250-300°C. It decreases somewhat (81-82%) at 350-400°C and then increases again up to ca. 90% at 450-500°C. Another product found is di-tert-butylbenzene. The concentration of this compound is only about 3 mole % at 250°C but it increases with increase in temperature and reaches a maximum of about 10 mole % in the range of 350-400°C. As temperature is increased further to 500°C, the amount of this dialkylated product again decreases to around 4%. Small amounts of toluene, ethylbenzene, styrene and cumene are also observed in the liquid product.

In the 250-400°C range, the gaseous product (Figure 1b) consists mainly (ca. 96% at 350°C) of  $C_4$  hydrocarbons, i.e., isobutane and isobutene. At 500°C the concentration of  $C_4$  compounds decreases sharply to about 43% of the total gas, with the balance (57%) composed of  $C_1$ - $C_3$  gases, in particular methane (33%).

Table 2 and Figures 2a and 2b summarize the change in product composition from  $ZnCl_2$ -catalyzed hydrodealkylation of isopropylbenzene (2) as a function of reaction temperature (200-450°C), keeping a constant reaction time of 90 seconds and a hydrogen pressure of 850 psig. As seen from Table 2 and Figure 2a, the conversion of compound 2 increases with increase in temperature (from only 0.5 at 200°C to 38.4% at 450°C). Further, there is a marked change in liquid product composition with increasing temperature. At 200°C the main liquid products are ethylbenzene and styrene (69%) but as temperature is increased to 250°C the concentration of these compounds decreases, while that of benzene increases. With further increase in temperature (300-450°C) the reaction selectivity increases and benzene becomes the predominant liquid product (ca. 86% between 350-450°C). The composition of the gaseous product (Figure 2b) also changes markedly with temperature. Thus, at 200°C methane is the major product (ca. 60%) but as temperature is increased the concentration of this compound decreases sharply and the predominant gaseous products become propane and propylene (concentration of  $C_3$  gases, ca. 83% at 300-350°C). It should be noted that under identical conditions the conversion of isopropylbenzene, 2 is considerably lower than that of t-butylbenzene, 1 (Table 1). This indicates a higher hydrodealkylation rate for 1, as compared to 2.

Table 3 and Figures 3a and 3b summarize the change in product composition from  $ZnCl_2$ -catalyzed hydrodealkylation of sec-butylbenzene (3) as a function of reaction temperature (200-450°C), keeping a constant reaction time of 90 seconds and a hydrogen pressure of 850 psig. As seen from Table 3 and Figure 3a, the conversion of 3 increases with increase in Temperature from 1.2 at 200°C to ca. 46% at 450°C. Further, it is seen that the liquid product composition changes drastically with temperature. Thus the main liquid products at 200°C are ethylbenzene and styrene, but as temperature increases, the concentration of these products drops sharply while the anticipated dealkylation product, i.e., benzene, becomes the predominant product. At 300°C benzene

comprises 96% of the liquid product but its concentration decreases at higher temperature. Other products of some importance are cumene and n-propylbenzene. Figure 3b shows that the main gases produced at 200°C are ethane and ethylene (92%). However, as temperature is increased to 300-400°C these products decrease sharply while the concentration of C<sub>4</sub> gases (isobutane, isobutene, n-butane, and n-butenes) increases up to ca. 89% at 350°C. As temperature is further increased to 450°C the yield of C<sub>4</sub> gases drops off and the concentration of lighter gases, i.e., C<sub>1</sub>-C<sub>3</sub>, increases apparently as a result of secondary cracking reactions.

Tables 1-3 contain also results obtained in experiments without the silica-gel supported ZnCl<sub>2</sub> catalyst (see separate columns in the right-hand side of Tables 1-3). In these experiments only silica-gel support was used as a contact material, keeping otherwise the same reaction conditions, i.e., sample size, hydrogen pressure and reaction time, as in the catalytic experiments. As seen from Table 1 the noncatalytic conversion of 1 at 300°C and 350°C (expts. 213 and 164, respectively) is very low (ca. 7%) as compared to that in the corresponding catalytic experiments (yields, 22.0% in expt. 166, and 42.1% in expt. 141 at 300° and 350°C, respectively). Further, it is seen from Table 1 that there is a lower selectivity for dealkylation in the non-catalytic experiments, as reflected in the lower concentration of benzene in the liquid product, and competitive formation of toluene as a side-chain dealkylation product.

Table 2 (right-hand column) shows the product composition from 2 in the noncatalytic experiments at 300° and 350°C (expts. 175 and 157, respectively). As in the case of compound 1 the conversion (ca. 4%) is much lower than that in the corresponding catalytic experiments. There is also a fundamental difference in liquid product composition. The main liquid products in the non-catalytic experiments are ethylbenzene and styrene (ca. 87%), while the predominant liquid product found at the corresponding temperatures in the catalytic experiments was benzene. Further, the main gas produced in the noncatalytic experiments is methane (ca. 90%), whereas the main gaseous products in the catalytic experiments are propane and propylene (ca. 82%).

Table 3 (right-hand column) provides the product composition of 3 at 350°C, using only the silica-gel support. As seen, the conversion is very low (ca. 6%) as in the case in compounds 1 and 2. The conversion of 3 at 350°C using the silica-gel supported ZnCl<sub>2</sub> catalyst is significantly higher (13.1%). The liquid products also show a major difference in composition. There is only ca. 20% of benzene formed in expt. 159 along with other compounds, i.e., toluene (ca. 34%), ethylbenzene and styrene (ca. 43%). In contrast, the main liquid product from the corresponding catalytic experiments at 350°C (expt. 155) is benzene (91%). Further, the composition of gaseous products shows major differences. In the noncatalytic experiment, methane ethane and ethylene are the major gaseous products (ca. 46%, 31% and 20%, respectively). In contrast, in the corresponding catalytic experiment C<sub>4</sub> paraffins and olefins are the main products produced (ca. 89%).

The significance of the results obtained will be discussed, together with other data, in the next report.

#### Future Work

Studies concerned with the preparation of porous coals needed for application of homogeneous catalysts in low-temperature coal liquefaction, will be continued.

TABLE 1

Change in Product Composition from Hydroalkylation of t-Butylbenzene (1) as a Function of Reaction Temperature

Experiment No.	167	166	141	142	143	168	213	164
Reaction temperature, °C	250	300	350	400	450	500	300 <sup>c</sup>	350 <sup>c</sup>
Conversion of <u>1</u> , mole %	4.4	22.0	42.1	50.1	58.1	68.6	0.7	0.6
Catalyst	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	none	none
Catalyst, wt. %	7.0	6.3	7.8	8.0	7.0	7.5	0.0	0.0

Gaseous Product Component,

mole % <sup>d</sup>								
CH <sub>4</sub>	0.8	0.5	0.8	2.5	13.5	33.0		Not determined <sup>e</sup>
C <sub>2</sub> H <sub>6</sub>	0.6	0.1	0.4	0.9	2.6	9.2		
C <sub>2</sub> H <sub>4</sub>	0.4	0.3	0.5	0.7	1.0	1.5		
C <sub>3</sub> H <sub>8</sub>	1.0	0.4	0.8	2.8	6.5	11.4		
C <sub>3</sub> H <sub>6</sub>	1.6	1.0	1.3	2.4	3.3	3.2		
<u>i</u> -C <sub>4</sub> H <sub>10</sub>	66.3	69.7	75.7	66.7	50.8	27.1		
<u>n</u> -C <sub>4</sub> H <sub>10</sub>	1.0	1.1	1.7	2.8	3.6	4.5		
Isobutene	25.7	23.4	17.7	17.0	14.8	8.6		
1-Butene	-----	1.2	1.1	1.7	1.8	-----		
2-Butene	2.6	2.3	-----	2.2	2.2	1.5		

Liquid Product Component,

mole % <sup>d</sup>								
Benzene	95.0	94.0	81.0	83.0	86.2	89.8	44.3	59.0
Toluene	2.0	1.3	1.6	2.1	2.0	4.3	31.2	25.6
Ethylbenzene	-----	0.1	1.6	2.1	2.1	-----	0.6	-----
Styrene	-----	0.1	1.1	1.8	1.2	1.5	2.4	0.3
Cumene	-----	-----	3.9	1.4	1.7	0.1	0.5	-----
Polyalkylated benzenes <sup>f</sup>	3.3	4.4	10.4	9.6	7.0	4.0	(21.0) <sup>g</sup>	(15.1) <sup>g</sup>

<sup>a</sup>In each run were used 0.15g (.001 mole) of 1 and 0.05g of 5% ZnCl<sub>2</sub>/SiO<sub>2</sub> catalyst. <sup>b</sup>Hydrogen pressure, 850 psig; total reaction time, 90 sec. <sup>c</sup>Blank experiments in the absence of catalyst, keeping all other conditions identical (footnotes a and b). <sup>d</sup>Moles per 100 mole of reacted feed 1; <sup>e</sup>Gas composition was not determined due to the very low conversion. <sup>f</sup>Mostly di-t-butylbenzene. <sup>g</sup>Unidentified condensation products

YIELD, MOLE/100 MOLE REACTED FEED

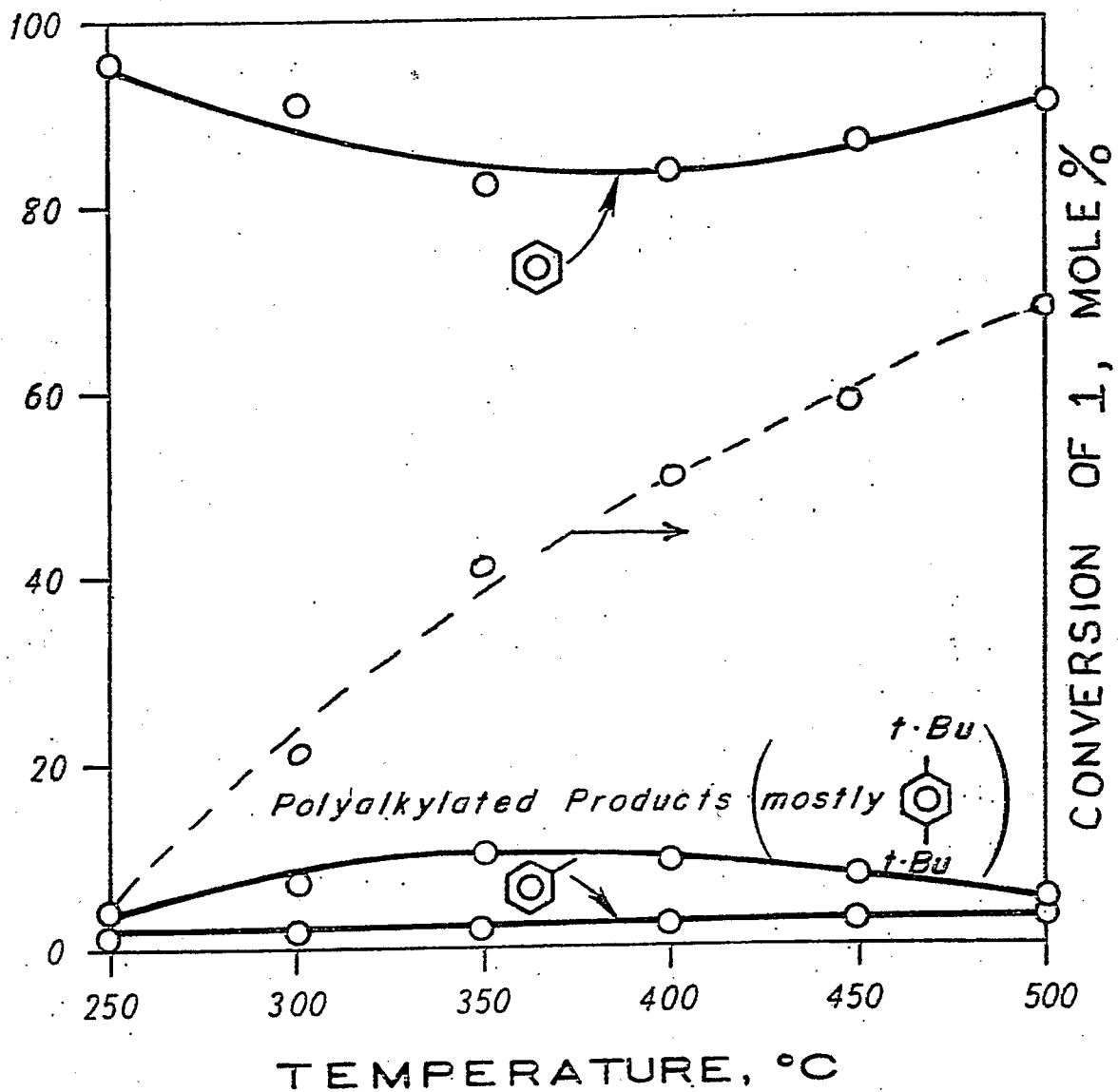


Fig. 1a. Change in Liquid Product Composition from Hydrodealkylation of t-Butylbenzene as a Function of Reaction Temperature

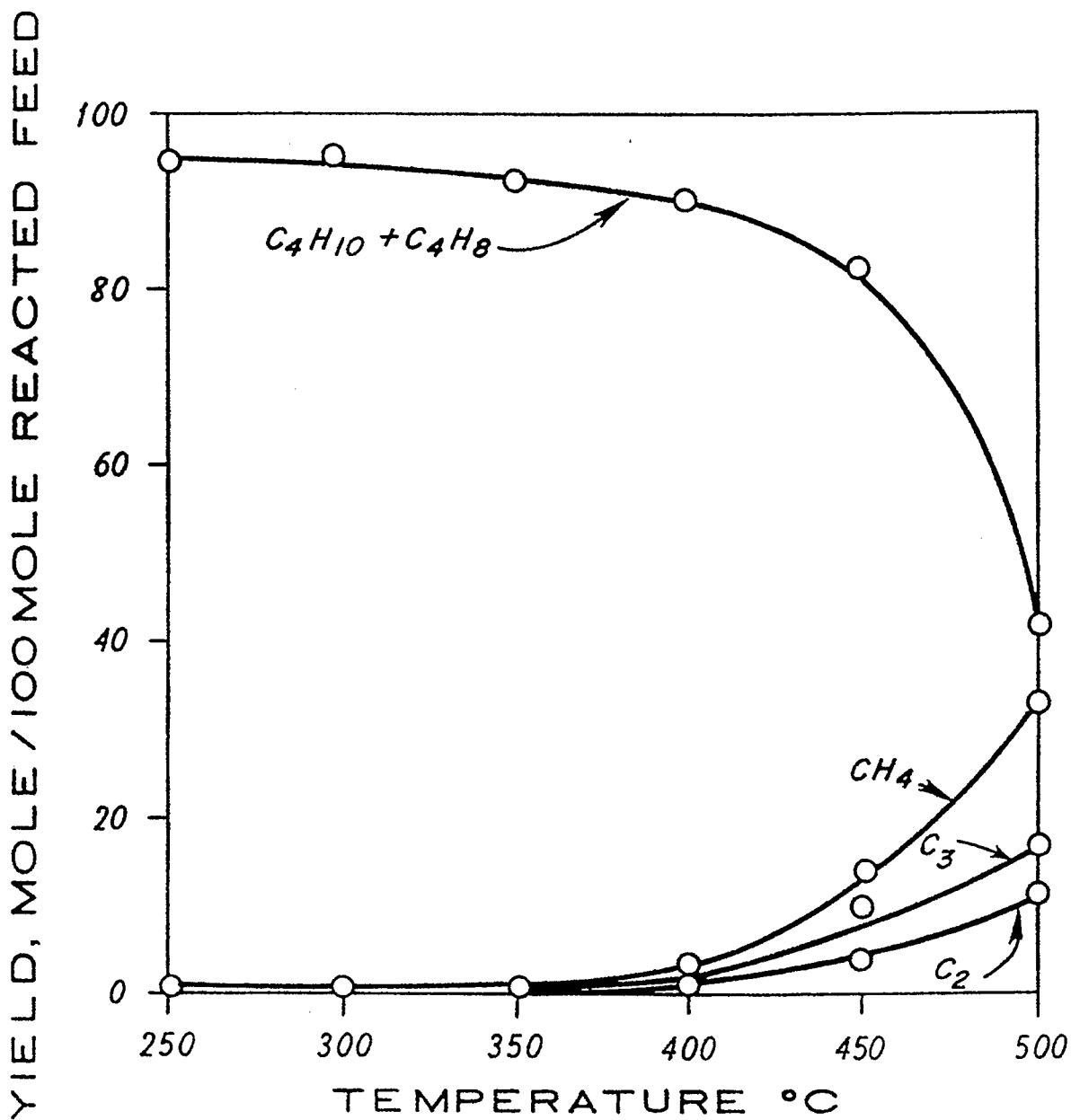


Fig. 1b. Change in Gas Product Composition from Hydrodealkylation of *t*-Butylbenzene as a Function of Reaction Temperature

TABLE 2

Change in Product Composition from Hydrodealkylation of Isopropylbenzene (2) as a Function of Reaction Temperature

Experiment No.	174	173	171	156	172	216	175	157
Conversion of 2, mole %	0.5	1.0	2.1	8.5	20.9	38.4	0.4	0.4
Reaction temperature, °C	200	250	300	350	400	450	300 <sup>c</sup>	300 <sup>c</sup>
Catalyst	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	none	none
Catalyst, wt. %	6.8	7.3	7.6	7.7	8.5	7.5	0.0	0.0
Gaseous Product Component, mole % <sup>d</sup>								
CH <sub>4</sub>	60.5	22.1	4.5	1.5	7.0	9.5	89.5	90.1
C <sub>2</sub> H <sub>6</sub>	0.2	-----	0.3	0.2	2.2	3.2	-----	-----
C <sub>2</sub> H <sub>4</sub>	1.6	1.4	1.0	0.4	1.4	1.1	-----	-----
C <sub>3</sub> H <sub>8</sub>	11.9	16.2	22.3	32.4	34.1	38.5	2.9	3.2
C <sub>3</sub> H <sub>6</sub>	19.7	50.4	61.1	50.0	36.9	31.1	4.8	5.1
i-C <sub>4</sub> H <sub>10</sub>	6.0	9.8	10.8	13.4	16.8	12.4	2.9	1.6
n-C <sub>4</sub> H <sub>10</sub>	-----	-----	-----	-----	1.7	1.7	-----	-----
Isobutene	-----	-----	-----	-----	-----	2.0	-----	-----
1-Butene	-----	-----	-----	-----	-----	0.2	-----	-----
2-Butene	-----	-----	-----	-----	-----	0.3	-----	-----
Liquid Product Component, mole % <sup>d</sup>								
Benzene	9.9	55.2	76.8	86.1	82.4	86.4	12.8	13.5
Toluene	20.7	8.8	7.4	5.9	6.7	2.0	0.6	0.8
Ethylbenzene	69.3	36.0	15.8	8.0	8.8	3.2	88.4	85.7
Styrene	-----	-----	-----	-----	2.2	0.4	-----	-----
Polyalkylated products <sup>e</sup>	-----	-----	-----	-----	-----	8.0	-----	-----

<sup>a</sup>In each run were used 0.15g (.001 mole) of 2 and 0.05g of 5% ZnCl<sub>2</sub>/SiO<sub>2</sub> catalyst. <sup>b</sup>Hydrogen pressure, 850 psig;<sup>c</sup>Blank experiments in the absence of catalyst, keeping all other conditions identical (footnotes a and b). <sup>d</sup>Moles per 100 mole of reacted feed 2; <sup>e</sup>Mostly di-isopropylbenzene

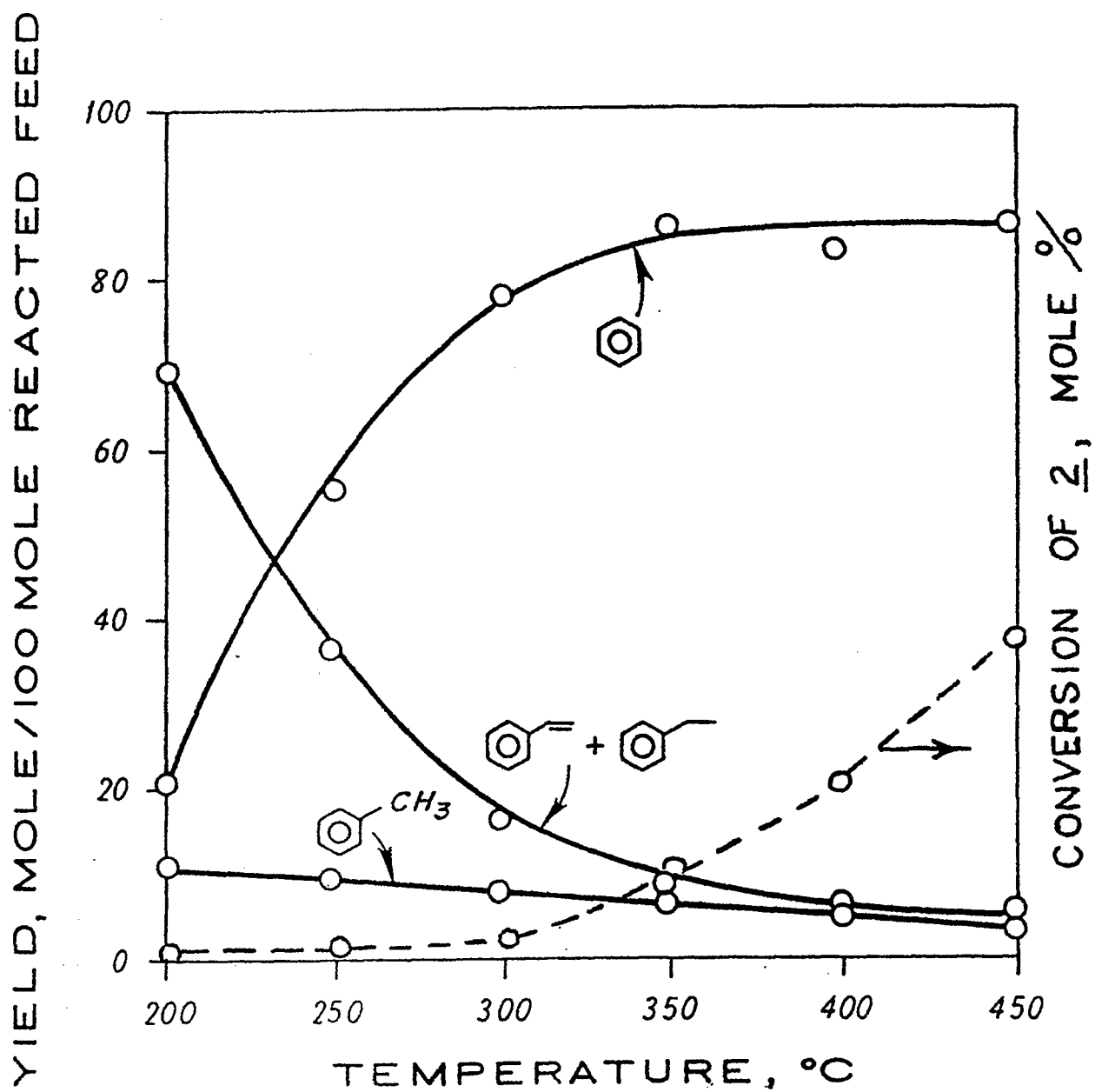


Fig. 2a. Change in Liquid Product Composition from Hydrodealkylation of Isopropylbenzene as a Function of Reaction Temperature

YIELD, MOLE/100 MOLE REACTED FEED

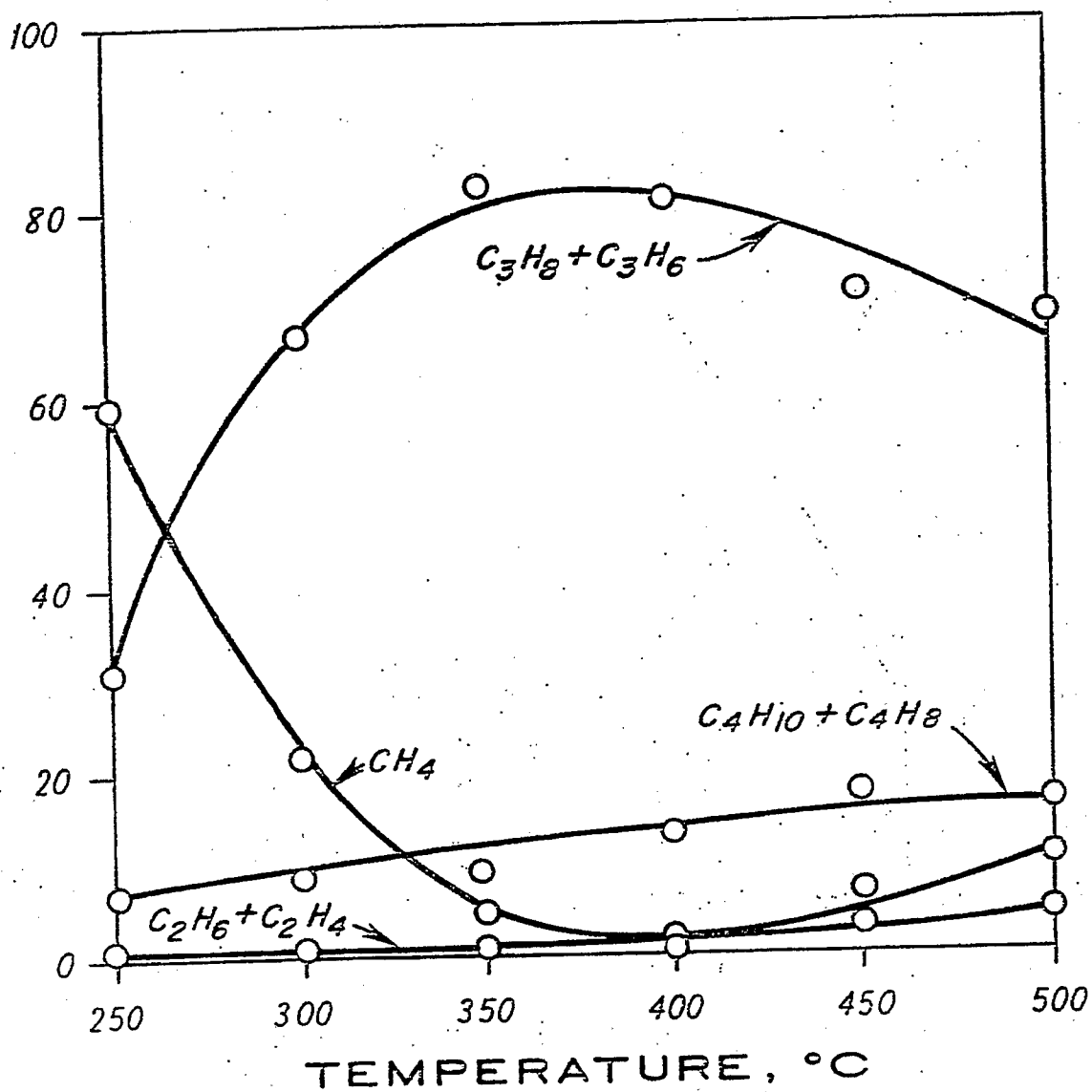


Fig. 2b. Change in Gas Product Composition from Hydrodealkylation of Isopropylbenzene as a Function of Reaction Temperature



Change in Product Composition from Hydrodealkylation of Sec-Butylbenzene (3) as a function of Reaction Temperature

Experiment No.	176	177	178	155	180	215	159	179
Reaction temperature	200	250	300	350	400	450	350 <sup>c</sup>	350 <sup>d</sup>
Conversion of <u>3</u> , mole %	1.2	1.8	4.8	13.1	30.0	45.5	0.6	4.1
Catalyst	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	none	Al <sub>2</sub> O <sub>3</sub>
Wt. % Catalyst	6.4	6.0	6.2	5.9	6.3	7.7	0.0	10.0
Gaseous Product								
Component, mole % <sup>e</sup>								
CH <sub>4</sub>	5.5	6.0	3.0	2.8	10.1	20.8	46.4	51.3
C <sub>2</sub> H <sub>6</sub>	70.8	32.0	20.7	3.9	4.22	4.9	31.3	29.3
C <sub>2</sub> H <sub>4</sub>	21.2	8.0	6.3	2.4	2.7	3.3	19.9	16.1
C <sub>3</sub> H <sub>8</sub>	0.3	0.1	0.2	0.9	4.8	5.5	0.2	0.1
C <sub>3</sub> H <sub>6</sub>	-----	0.3	0.3	0.9	1.9	2.0	0.4	1.0
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.3	24.2	52.2	64.0	52.3	31.6	0.2	0.1
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	1.5	6.5	2.9	4.5	6.0	6.5	0.9	0.9
Isobutene	0.4	14.5	15.8	16.4	11.6	0.5	0.7	0.6
1-Butene	-----	4.8	5.1	4.2	3.1	3.5	-----	-----
2-Butene	-----	-----	-----	-----	3.3	6.4	-----	0.7
Liquid Product								
Component mole % <sup>e</sup>								
Benzene	0.3	93.0	95.7	91.0	86.0	87.4	19.7	5.2
Toluene	0.2	2.2	3.3	2.0	3.8	1.7	34.0	63.5
Ethylbenzene & Styrene	99.5	4.8	0.9	4.3	7.8	4.0	42.9	21.8
<i>n</i> -propylbenzene & Styrene	-----	-----	-----	2.8	2.5	7.0	3.3	10.0

<sup>a</sup>In each run were used 0.15g (.001 mole) of 3 and 0.05g of 5% ZnCl<sub>2</sub>/SiO<sub>2</sub> catalyst. <sup>b</sup>Hydrogen pressure, 850 psig; Total reaction time, 90 sec. <sup>c</sup>Blank experiment in the absence of catalyst, keeping all other conditions identical (footnotes a and b). <sup>d</sup>Al<sub>2</sub>O<sub>3</sub> catalyst, 10% by wt. keeping all other conditions identical (footnotes a and b). <sup>e</sup>Moles per 100 mole of reacted feed 3.

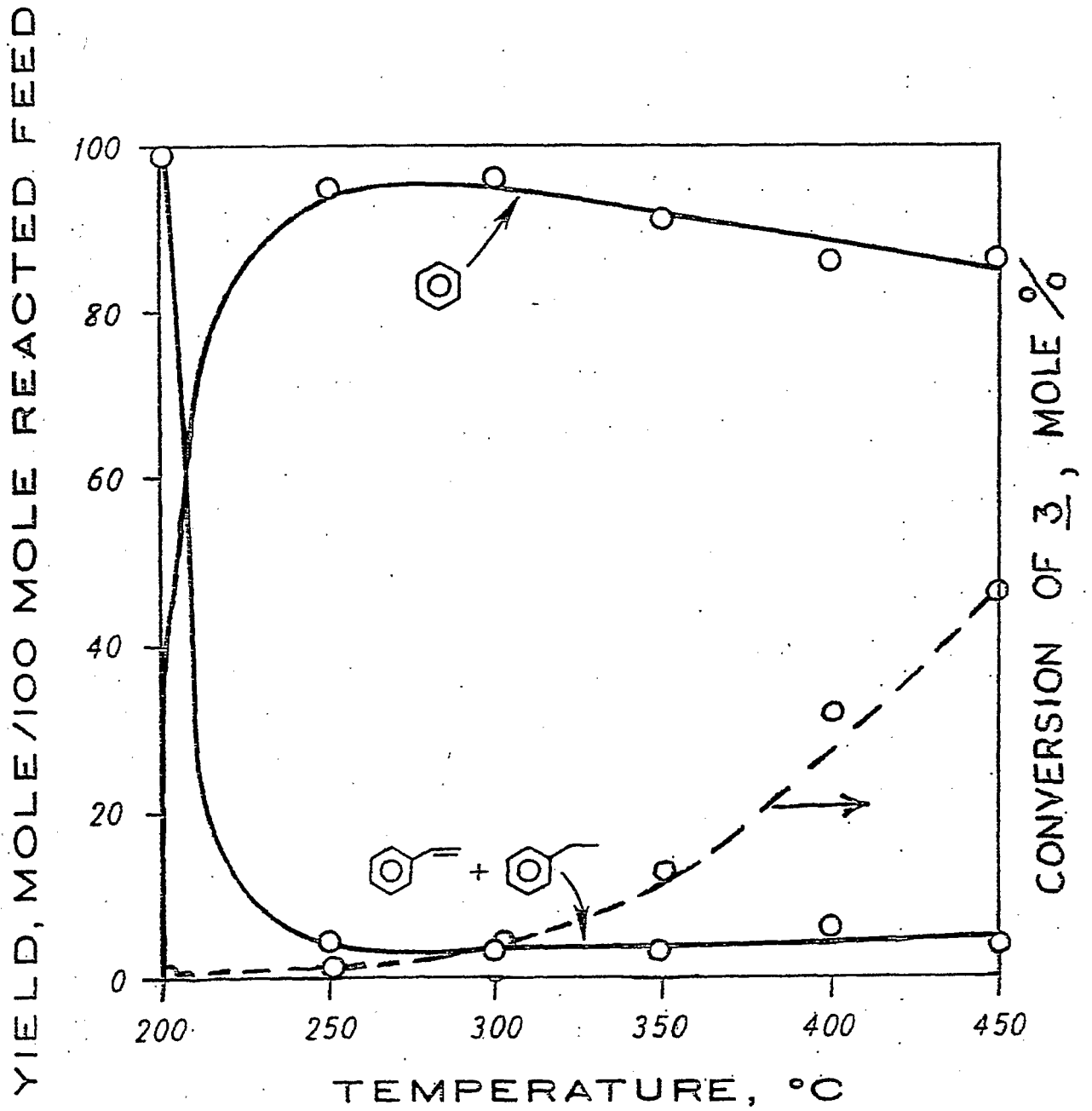


Fig. 3a. Change in Liquid Product Composition from Hydrodealkylation of sec-Butylbenzene as a Function of Reaction Temperature

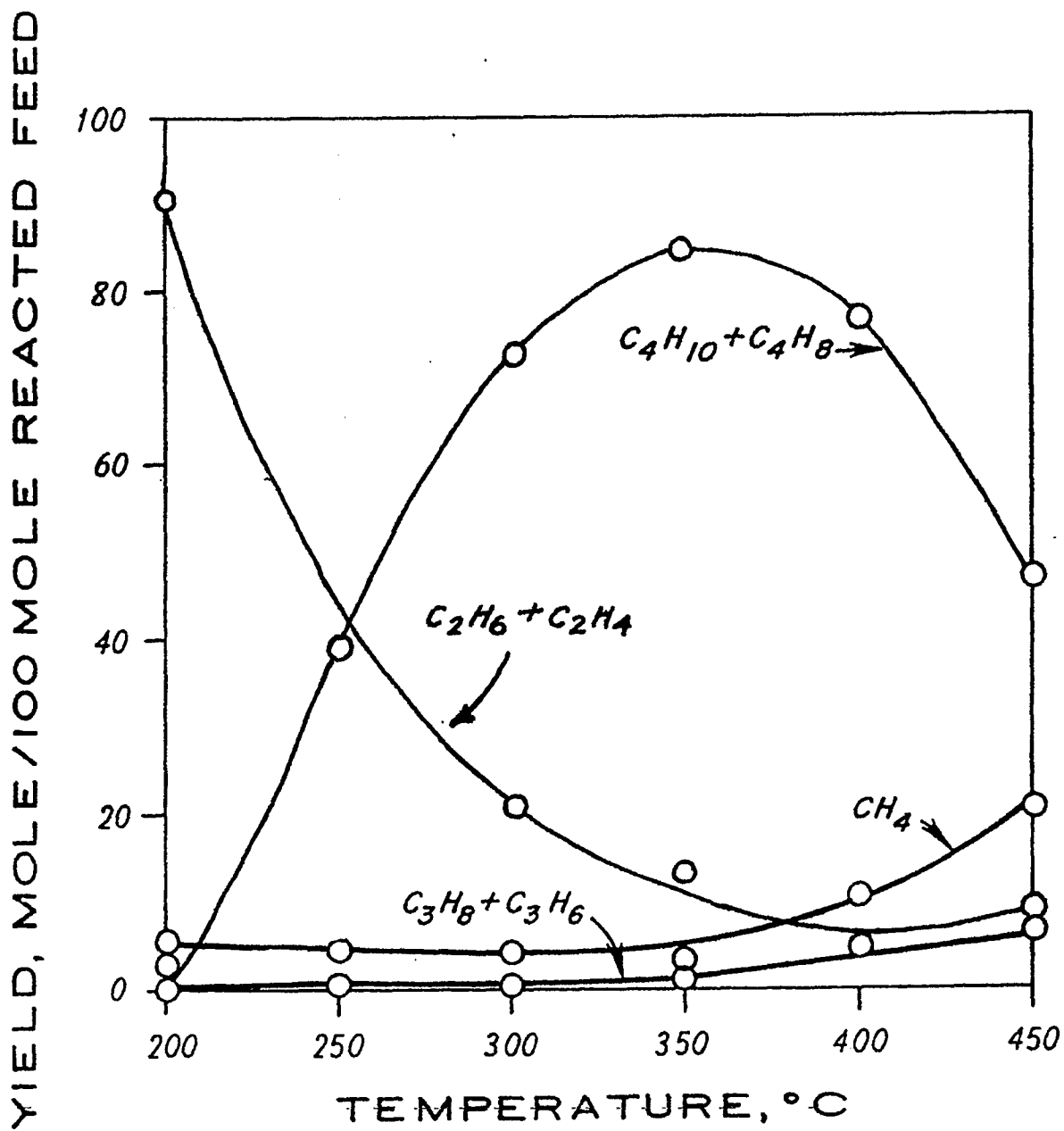


Fig. 3b. Change in Gas Product Composition from Hydrodealkylation of sec-Butylbenzene as a Function of Reaction Temperature

Task 2

Carbon-13 NMR Investigation of CDL and Coal

Faculty Advisor: R.J. Pugmire  
Post-Doctoral Fellow: D.K. Darling

A project report was not submitted on this task.

## Task 3

### Catalysis and Mechanism of Coal Liquefaction

Faculty Advisor: D.M. Bodily  
Graduate Student: Jason Miller

#### Introduction

The hydroliquefaction of coal may be characterized by a mechanism which involves the initial rupture of covalent bonds to form reactive intermediates. These intermediates may be stabilized by hydrogen transfer to form lower molecular weight products or they may polymerize to form insoluble char or coke. Metal halides such as zinc chloride have been shown to be active in the bond scission stage of the reaction where as many catalysts are active only in stabilizing the intermediates, often by regenerating a hydrogen donor. The combination of thermal and catalytic reactions occurring simultaneously results in a complicated reaction mechanism. The chemistry of  $ZnCl_2$  will be studied with model compounds and coal by such reactions as hydrogen transfers, cleavage of specific bonds and interaction with  $\pi$  electron systems.

A high performance liquid chromatograph, HPLC, will be used to analyze liquid products of the reactions under study. Further characterization of the products will be by nuclear magnetic resonance, NMR, structural analysis and vapor pressure osmometry.

#### Project Status

Research is continuing on the characterization of the CDL fractions obtained from initial separation techniques. Retention time tagging of standards and standards mixtures has progressed. Progress has been slowed by slow chemical delivery and then by the solvent delivery system failure. Repairs were pending parts delivery and will be completed soon.

#### Future Work

Better raw separation techniques and liquid sample preparation and handling techniques will be developed. Other experiments will use GPC on various fractions generated by improved separation procedures. Problems involving compound retention by columns will be minimized through further experiments. The literature survey will continue to update HPLC procedures for optimization of separation procedures and characterization of the resulting fractions.

## Catalysis and Mechanism of Coal Liquefaction

### Catalytic Action of Zinc Chloride in Short-Residence Coal Hydrogenation

Faculty Advisor: David M. Bodily

#### Introduction

Metal halides such as  $ZnCl_2$  are well-known to be active catalysts for coal hydrogenation. Zinc chloride has been shown to be a very effective catalyst for coal hydrogenation in the entrained-flow reactor developed at the University of Utah.<sup>1,2</sup> Bell and co-workers<sup>3-5</sup> have studied the reactions of model compounds with  $ZnCl_2$  under conditions similar to those employed in coal hydrogenation. They observed cleavage of C-O and C-C bonds in the model compound and proposed that the active catalytic species is a Bronsted acid formed from  $ZnCl_2$ .

Shibaoka, Russell and Bodily<sup>6</sup> proposed a model to explain the liquefaction of coal, based on microscopic examination of the solid products from metal halide catalyzed coal hydrogenation. The model involves a competition between hydrogenation and carbonization reactions. The hydrogenation process starts at the surface of vitrinite particles and progresses toward the center. The vitrinite is converted to a plastic material of lower reflectance, which is the source of oils, asphaltenes and preasphaltenes. Concurrently, carbonization occurs in the center of the particles, resulting in vesiculation and a higher reflectance material. The partially carbonized material can be hydrogenated at later stages, but at a lower rate than the original coal.

Thermal and/or catalytic bond rupture occurs during the liquefaction process. The initial products of the bond cleavage reactions may be stabilized by hydrogen addition, resulting in cleavage of bridges between aromatic ring systems and in dealkylation of aromatic rings. If the initial products of the reaction are not stabilized, they may polymerize to form semicoke-like material. This primary semicoke may be isotropic or exhibit a fine-grained anisotropic mosaic texture, depending on the rank of the coal. The plastic material formed by stabilization of the initial products may be further hydrogenated or, under hydrogen deficient conditions, may form secondary semicoke. The secondary semicoke is of medium to course-grained anisotropic mosaic texture. Bodily and Shibaoka<sup>7</sup> used this model to explain the nature of the residues from hydrogenation in the short-residence, entrained-flow hydrogenation reactor. The role of the  $ZnCl_2$  catalyst is examined in this study.

#### Project Status

Clear Creek, Utah coal (45.4% VM, 0.8% moisture and 6.5% ash) was hydrogenated in the short-residence time, entrained-flow reactor under a previous contract.<sup>8</sup> The conversion results have been reported.<sup>9</sup> The initial stages of the reaction were studied by lowering the temperature or the length of the reactor. Several catalyst systems were employed.

The solid residues of the reaction were examined by optical microscopy, electron microscopy and electron microprobe techniques. The results of the study may be summarized under the following points:

1 - Zinc chloride lowers the temperature at which softening occurs. Upon softening, the coal agglomerates and is retained in the reactor for up to several minutes. Coals which do not soften and agglomerate in the initial stages of the reaction are blown quickly through the reactor and show only evidence of primary semicoke formation. Reactions at short reactor length at 500°C or at 450°C with longer reactors demonstrate that the plastic margin of the partially hydrogenated coal grains serves as a glue to cause agglomeration. Softening is thought to occur by cleavage of covalent bonds in bridges between aromatic ring systems. Zinc chloride is thus active in this step of the liquefaction reaction.

2 - The hydrogen donor capability of the coal (hydroaromatic content) is important in stabilizing the products of the initial reaction. Fluidity of the product is thought to be important in relation to the diffusion of donor species and thus to have an important effect on reaction time and conversion.

3 - Solvents preferentially extract from the hydrogenated regions. Toluene extracts from the low-reflectance regions, but there is no indication of extraction from the higher-reflectance regions.

4 - The catalyst is altered during the reaction. Most of the chlorine is extracted by pyridine, although zinc remains in the particles. Zinc is often found in the same regions as sulfur, although no compounds have been identified. Previous studies have shown that ZnS is not an effective catalyst.

5 - The catalyst is dispersed through the coal as the coal softens. After impregnation it is found only on the surface.

6 - Red mud plus sulfur and presulfided red mud coat the surface of the coal particles but do not catalyze the softening reactions. Cobalt molybdate on alumina also does not catalyze the softening reaction and is found as separate particles in the residues.

#### Future Work

This study was performed by Professor Bodily while on sabbatical leave in the laboratories of CSIRO, Division of Fossil Fuels, North Ryde, Australia. The study will continue as time and manpower is available.

#### References

1. R.E. Wood and W.H. Wiser, Ind. Eng. Chem., Proc. Design Devel., **15**, 144 (1976).
2. J.M. Lytle, R.E. Wood and W.H. Wiser, Fuel, **59**, 471 (1980).

3. D.P. Mobley and A.T. Bell, Fuel, 58, 661 (1979).
4. N.D. Taylor and A.T. Bell, Fuel, 59, 499 (1980).
5. D.P. Mobley and A.T. Bell, Fuel, 59, 507 (1980).
6. M. Shibaoka, N.J. Russell and D.M. Bodily, Fuel, submitted.
7. D.M. Bodily and M. Shibaoka, Fuel, submitted.
8. W.H. Wiser, "Applied Research and Evaluation of Process Concepts for Liquefaction and Gasification of Western Coal," Final Report, U.S. Department of Energy, Contract No. E(49-18)-2006, Sept 1980, p 184.
9. R. Yoshida and D.M. Bodily, Amer. Chem. Soc., Fuel Chem. Div., Preprints, 24 (2), 371 (1979).



## Task 5

### The Mechanism of Pyrolysis of Bituminous Coal

Faculty Advisor: W.H. Wiser  
Graduate Student: J.K. Shigley

#### Introduction

In the present state of knowledge concerning the fundamental chemistry of coal liquefaction in the temperature range 375-550°C, the liquefaction reactions are initiated by thermal rupture of bonds in the bridges joining configurations in the coal, yielding free radicals. The different approaches to liquefaction, except for Fischer-Tropsch variations, represent ways of stabilizing the free radicals to produce molecules. The stabilization involving abstraction by the free radicals of hydrogen from the hydro-aromatic structures of the coal is believed to be the predominant means of yielding liquid size molecules in the early stages of all coal liquefaction processes, except Fischer-Tropsch variations. The objective of this research is to understand the chemistry of this pyrolytic operation using model compounds which contain structures believed to be prominent in bituminous coals.

#### Project Status

Several variations of the originally planned experimental technique<sup>1</sup> were tried to correct the problems encountered with sample collection and plunger movement. After numerous unsuccessful attempts to correct these problems, it was decided to alter the experimental technique to remove the intrinsic sampling problems. To insure representative and accurate sampling and consistent analysis of reaction products, the samples will be flushed with helium (dried, filtered and oxygen free) directly into the gas chromatograph. A 4-port Valco switching valve will be used to insure continuous flow of helium through the gas chromatograph and optimum utilization of the gas chromatograph during downtime of the pyrolysis assemblies. The valve and all lines will be heated to prevent condensation of reaction products.

#### Future Work

Construction and assembly of the apparatus and connections will be completed. Various tests will be conducted to insure the integrity and operation procedure of the system. Problems have been anticipated with sample size with respect to column and detector overloading, injection consistency, backflushing of reaction products upon breaking reaction tube and product condensation in the lines from the pyrolysis assembly and the gas chromatograph.

#### Reference

1. W.H. Wiser et al., DOE Contract No. DE/ET/14700-5, Quarterly Progress Report, Salt Lake City, Utah, Sept-Dec 1980.

Catalytic Hydrogenation of CD Liquids and Related  
Polycyclic Aromatic Hydrocarbons

Faculty Advisor: J. Shabtai  
Research Associate: C. Russell

Introduction

The main objective of this research project is to develop a versatile process for controllable hydrotreating of highly aromatic coal liquids, viz., a process permitting production of naphthenic-aromatic feedstocks containing variable relative concentrations of hydroaromatic vs. aromatic ring structures. Such feedstocks, including the extreme case of a fully hydrogenated coal liquid, are suitable starting materials for catalytic cracking, as applied for preferential production of light liquid fuels. The overall objective of this project and of a parallel catalytic cracking study is, therefore, to develop and optimize a hydrotreating-catalytic cracking process sequence for conversion of coal liquids into conventional fuels.

The present project includes also a study of metal sulfide-catalyzed hydrogenation of model polycyclic arenes present in coal liquids, e.g., phenanthrene, pyrene, anthracene and triphenylene, as a function of catalyst type and experimental variables. This part of the study provides basic information on the rate, mechanism and stereochemistry of hydrogenation of structurally distinct aromatic systems in the presence of sulfided catalysts.

Project Status

This report provides data obtained in a kinetic study of the hydrogenation of triphenylene (1) in the presence of a sulfided Ni-W catalyst. Experiments were carried out using an autoclave system described elsewhere,<sup>1</sup> and modified to allow for withdrawing of samples during the hydrogenation reaction. Products were identified by a combination of gas chromatography-mass spectrometry, and by comparison with pure reference compounds. Samples taken in the kinetic runs were quantitatively analyzed by gas chromatography.

Kinetic rate constants were obtained for a reaction pressure of 2500 psi at three different reaction temperatures, i.e., 300°, 350° and 380°C. Figure 1 shows the change in product composition from hydrogenation of 1 as a function of time for a reaction pressure of 2500 psig and a reaction temperature of 300°C. Mathematical analysis of experimental results such as illustrated in Figure 1 provided the kinetic rate constants for the reaction. Figure 2 summarizes the hydrogenation network and the kinetic rate constants obtained for the consecutive hydrogenation steps involved in the conversion of 1 into perhydrotriphenylene.

The results obtained (Figure 2) indicate that at each temperature studied the rate constants for hydrogenation of the three peripheral rings

are in the order  $k_3 > k_2 > k_1$ . In other words the rate of hydrogenation increases with increase in the number of saturated rings in the partially hydrogenated intermediate compound. However, the rate constant for the last step ( $k_4$ ), involving hydrogenation of the central, hexasubstituted aromatic ring is sharply lower, apparently due to steric effects.<sup>2</sup> It is also found that the values of  $k_1$ ,  $k_2$  and  $k_3$  at 380°C are lower than the values of the corresponding constants at 350°C. The reason for this behavior, including the possibility of faster catalyst deactivation at 380°C, is presently under investigation.

#### Future Work

A kinetic study of the hydrogenation of pyrene has been initiated.

#### References

1. L. Veluswamy, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1977.
2. J. Shabtai, C. Russell, M. Ferster and A.G. Oblad, to be published.

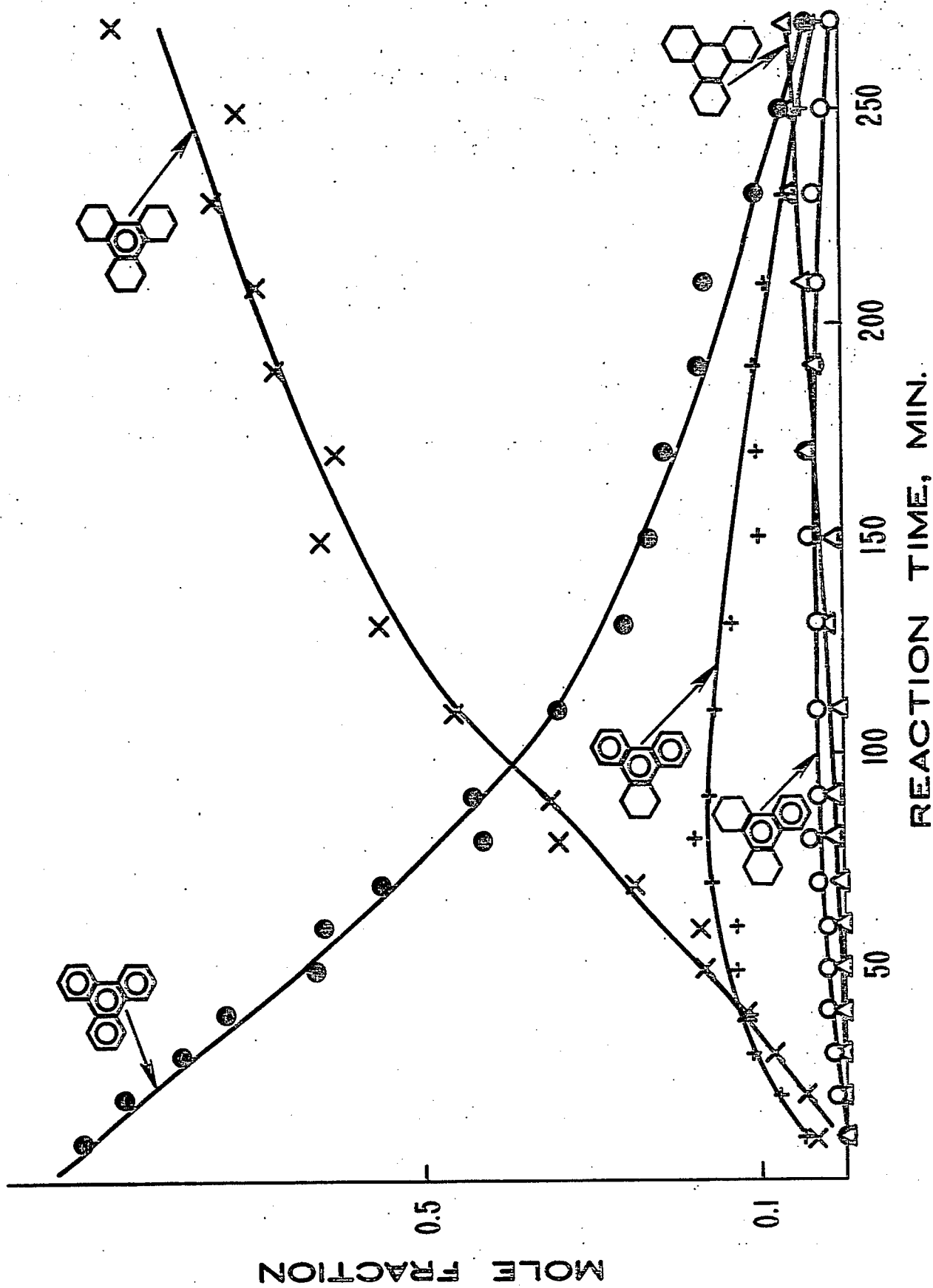


Figure 1. Change in product composition from hydrogenation of triphenylene (1) as a function of reaction time. (Catalyst: sulfided Ni-W/Al<sub>2</sub>O<sub>3</sub>; Pressure: 2500 psi; Temp.: 300°C)

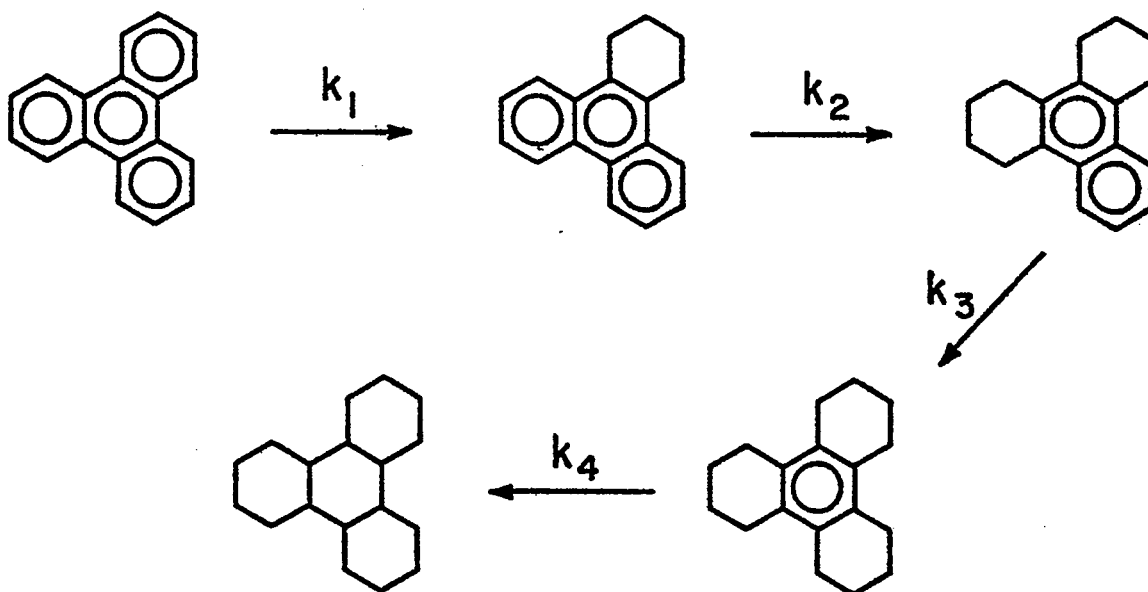


Figure 2. Hydrogenation of Triphenylene--Reaction Network

Rate constants,  $\text{min}^{-1}$   
 (Pressure: 2500 psi; catalyst: sulfided Ni-W/ $\text{Al}_2\text{O}_3$ )

$T, ^\circ\text{C}$	$k_1$	$k_2$	$k_3$	$k_4$
300	0.008	0.012	0.015	0.0004
350	0.036	0.115	0.255	0.002
380	0.024	0.04	0.10	0.003

## Task 7

### Denitrogenation and Deoxygenation of CD Liquids and Related N- and O- Compounds

#### Hydrodenitrogenation of Coal-Derived Liquids and Related N-Containing Compounds

Faculty Advisor: J. Shabtai  
C. Russell  
Graduate Student: J. Yeh

#### Introduction

The main objective of this research project is to develop effective catalyst systems and processing conditions for reductive hydrodenitrogenation (HDN), as well as for direct (nonreductive) denitrogenation of coal-derived liquids (CDL) in a wide range of nitrogen contents and structural type composition. This is of particular importance in view of the higher concentration of nitrogen-containing compounds in CDL as compared to that of petroleum feedstocks. For a better understanding of denitrogenation processes, the project includes systematic denitrogenation studies not only of CDL but also of related model N-containing compounds found in such liquids, e.g., phenanthridine, 1,10-phenanthroline, carbazoles, acridines, etc., as a function of catalyst type and experimental variables. A part of the study is concerned with determination of the rate, mechanism and stereochemistry of HDN of structurally distinct N-containing aromatic systems in the presence of sulfided catalysts.

#### Project Status

This report provides partial results obtained in an ongoing kinetic study of the hydrodenitrogenation of 7,8-benzoquinoline (1) in the presence of a sulfided Ni-W catalyst (precursor: Ni-W/Al<sub>2</sub>O<sub>3</sub>, Nalco Sphercat 550). Kinetic experiments were performed with an autoclave system described elsewhere,<sup>1</sup> and modified to allow for withdrawing of samples during the reaction. Products were identified by a combination of high resolution gas chromatography-mass spectrometry, and by comparison with reference compounds. Quantitative analyses were performed by gas chromatography.

Kinetic rate constants were obtained for a reaction pressure of 2500 psi at reaction temperatures of 250°C and 330°C (additional measurements at other temperatures, as well as studies with Co-Mo and Ni-Mo catalysts, are presently underway). Figure 1 summarizes the kinetic network and the kinetic rate constants obtained. The data indicate that after relatively fast saturation of the pyridine ring in 1 to yield 1,2,3,4-tetrahydro-7,8-benzoquinoline (2), the subsequent hydrogenation of the end aromatic ring in 2, to yield 1,2,3,4,9,10,11,12-octahydro-7,8-benzoquinoline (3) is faster than the HDN reaction of 2 leading to 2-propylnaphthalene (4) viz.,  $k_3 > k_2$ . It is also found that  $k_6 > k_5$  indicating that a major part of compound 3 undergoes further hydrogenation to perhydro-7,8-benzoquinoline, prior to the HDN step. These results demonstrate the high ring hydrogenation activity vs. relatively low C-N hydrogenolysis activity of sulfided Ni-W catalysts obtained from commercial precursors.

Initial results with sulfided Co-Mo catalysts indicate that the latter possess, generally a more satisfactory C-N hydrogenolysis activity. Newly designed Co-Mo catalysts, possessing augmented C-N hydrogenolysis activity vs. relatively low ring hydrogenation activity, are presently under development in this laboratory (Task 10). Such catalysts will be applied in the continuation of Task 6.

#### Future Work

The HDN kinetic studies of coal-derived liquids and related model compounds will be continued.

#### References

1. L. Veluswamy, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1977.

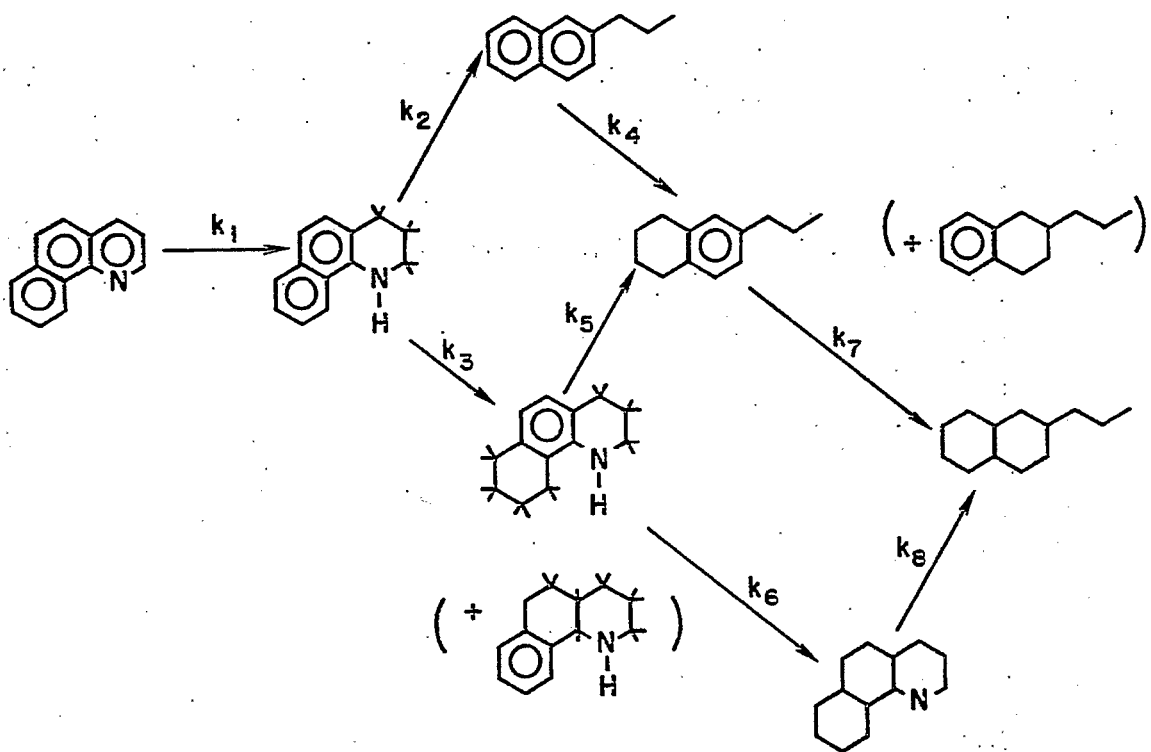


Figure 1.

Hydrogenation-HDN of 7,8-Benzoquinoline

Rate Constants,  $\text{min}^{-1}$

(hydrogen pressure, 2500 psig; catalyst: sulfided Ni-W/ $\text{Al}_2\text{O}_3$ )

Temp., °C	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$	$K_6$	$K_7$	$K_8$
250	0.010	<0.0001	0.0018	--	<0.0001	0.001	--	<0.001
330	0.033	0.001	0.006	<0.001	0.002	0.003	<0.001	ca 0.02



## Task 8

### Catalytic Cracking of Hydrogenated Coal-Derived Liquids and Related Compounds

Faculty Advisors: J. Shabtai  
A. G. Oblad  
Graduate Student: Z. Pai

#### Introduction

Hydrogenation followed by catalytic cracking provides a feasible process sequence for conversion of coal liquids into conventional fuels. Such a sequence has certain advantages in comparison with a hydrocracking-catalytic reforming scheme.<sup>1</sup>

The present project is concerned with the following interrelated subjects: (1) systematic catalytic cracking studies of polycyclic naphthenes and naphthoaromatics found in hydrogenated coal liquids and (2) systematic catalytic cracking studies of hydrotreated coal-derived liquids.

#### Project Status

In continuation of previous studies,<sup>1</sup> work is presently underway to prepare partially hydrogenated feeds derived from SRC-I and SRC-II products. These hydrotreated feeds have variable concentrations of naphthenic vs. aromatic ring structures, and therefore, allow for determination of catalytic cracking rates as a function of the depth of hydrogenation. Parallel to this, work is being carried out on the preparation of partially hydrogenated chrysenes, pyrenes, and other polycyclic arenes, to be used as model feedstocks in catalytic cracking studies.

This report provides data on the hydrogenation of chrysene over a sulfided Ni-W catalyst, using a batch autoclave system described elsewhere.<sup>2</sup> The hydrogen pressure applied was 2900 psig, and reaction temperature was varied from 250°C to 350°C. At a reaction temperature of 300°C, the reaction time was varied from 2 to 6 hours; while at 350°C the variation in reaction time was from 1 to 3 hours. The data obtained allow for selection of appropriate sets of reaction conditions suitable for preparation of specific partially hydrogenated chryzenes. For example, at a reaction temperature of 300°C, a reaction time of 2 hours and a hydrogen pressure of 2900 psig, 75% of the chrysene is converted, and more than 50% of the product consists of 1,2,3,4-tetrahydrochrysene. Further, at a reaction temperature of 300°C, a reaction time of 6 hours and a hydrogen pressure of 2900 psig, the chrysene is fully converted to yield a product containing 55% of 1,2,3,4,5,6,7,8,9,10,17,18-dodecahydrochrysene, and 41% of perhydrochrysene. The desired pure model compounds are presently being isolated from the products by fractional distillation under vacuum.

### Future Work

The preparation of (a) partially hydrogenated SRC-I and SRC-II products; and (b) partially hydrogenated polycyclic arenes will be continued. Catalytic cracking studies with such feedstocks will be carried out.

### References

1. S. Sunder, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1980.
2. L. Veluswamy, Ph.D. Thesis, University of Utah, 1977.

## Task 9

### Hydropyrolysis (Thermal Hydrocracking) of CD Liquids

Faculty Advisors: J. Shabtai  
A.G. Oblad  
Graduate Student: Y. Wen

#### Introduction

This project is concerned with a systematic investigation of hydro-pyrolysis (thermal hydrocracking) as an alternative processing concept for upgrading of heavy coal-derived liquids into light liquid products. The high efficiency and versatility of hydro-pyrolysis has been indicated in previous studies with heavy CDL feedstocks and with model compounds.<sup>1-3</sup> The present project is an extension of this previous work for the purpose of (a) further developing and enlarging the scope of the hydro-pyrolytic reaction, and (b) optimizing the operating conditions for different types of feedstocks, e.g., coal liquids from different liquefaction processes, partially hydrotreated coal liquids, and relevant model compounds. The project includes systematic studies of reaction kinetics, product composition, and coking tendencies, as a function of operating variables. The work with model compounds provides necessary data for further elucidation of mechanistic aspects of the hydro-pyrolysis process.

#### Project Status

A new and improved hydro-pyrolysis unit has been designed, and is presently under construction. A flow diagram of the unit and a description of its component parts is given in Figure 1.

#### Future Work

The construction of the new hydro-pyrolysis unit will be completed and put in operation.

#### References

1. J. Shabtai, R. Ramakrishnan, and A.G. Oblad, *Advances in Chemistry*, No. 183, *Thermal Hydrocarbon Chemistry*, Amer. Chem. Soc., 1979, pp 297-328.
2. R. Ramakrishnan, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1978.
3. A.G. Oblad, J. Shabtai and R. Ramakrishnan, pending patents.

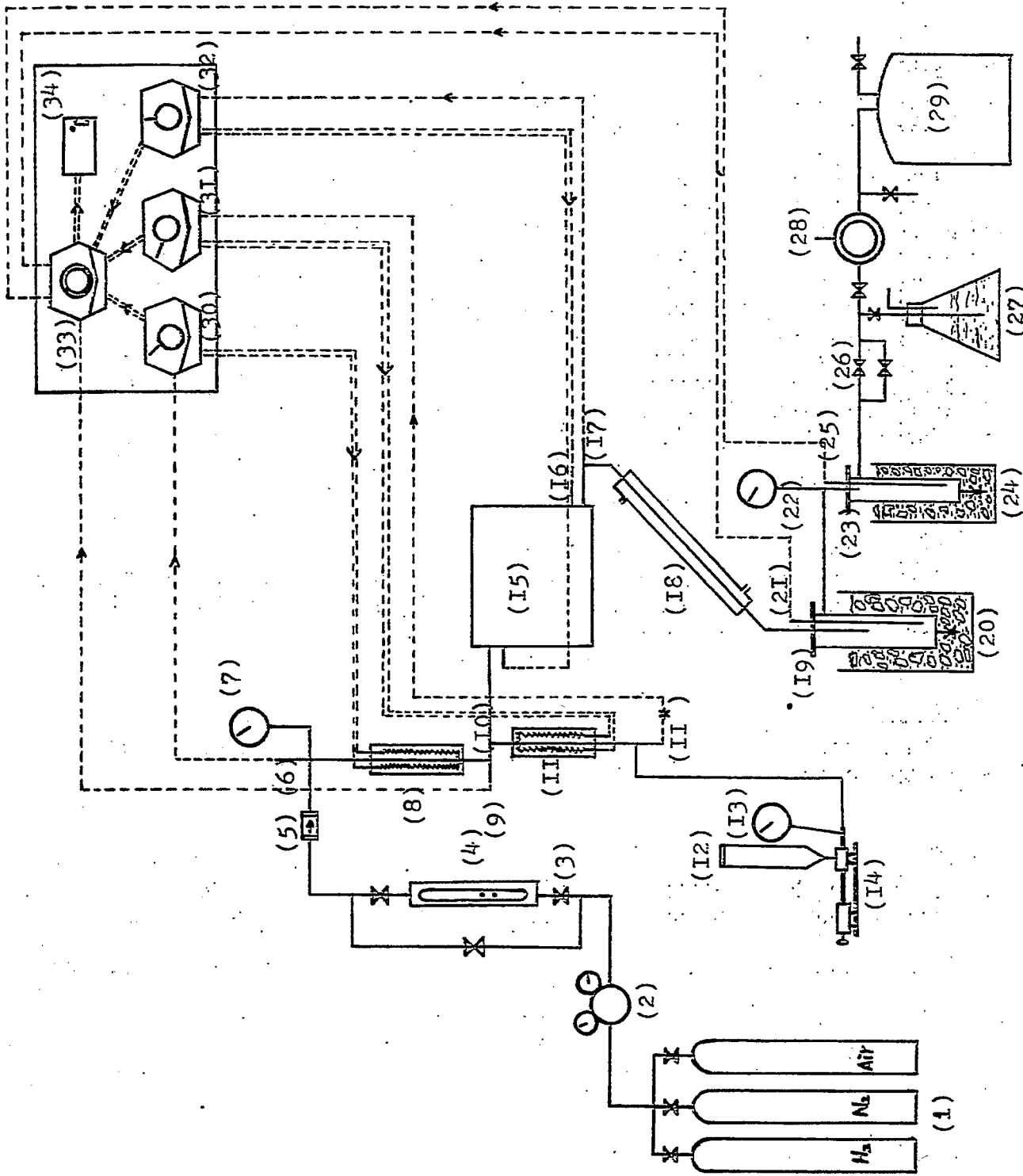


Figure 1. Flow Diagram of Hydrolysis Unit.

## Hydropyrolysis Unit — Components

<u>No.</u>	<u>Component</u>	<u>Description</u>
1	cylinders	max. 3500 psi
2	regulator	
3	meter valve	control hydrogen flow
4	rotameter	
5	check valve	one way
6	thermocouple	measure preheated H <sub>2</sub> gas temp
7	pressure gauge	reactor inlet pressure
8	heating element	preheating H <sub>2</sub> gas
9	thermocouple	detect mixed gas temp
10	mixer	mix feed and H <sub>2</sub> gas
11	heating element	preheating feed
11*	thermocouple	detect preheated feed temp
12	feed holder	
13	pressure gauge	pump pressure
14	meter pump	max. 250 ml
15	reactor	helical tube reactor
16	reactor heating element	tubular heating element (semi-circle with reactor tube)
17	thermocouple	detect reactor temp
18	condenser	2½" x 24"
19	gas-liquid separator	300 ml
20	ice-water holder	cooling the gas
21	thermocouple	detect 1st separator temp
22	pressure gauge	indicate outlet pressure
23	gas-liquid separator	120 ml
24	ice-water holder	cooling the light compound
25	thermocouple	detect 2nd separator temp
26	meter valve	control the system pressure
27	CdCl <sub>2</sub> scrubber	when use H <sub>2</sub> S gas to deactivate the reactor tube
28	wet test meter	calculate the gas volume
29	gas holder	500 liters
30	temperature controller	control the temp of preheated H <sub>2</sub> gas
31	temperature controller	control the temp of preheated feed
32	temperature controller	control the reactor temp
33	RTD switch	
34	digital temp indicator	

Systematic Structural Activity Study of Supported  
Sulfide Catalysts for Coal Liquids Upgrading

Faculty Advisors: F.E. Massoth  
J. Shabtai

Post-Doctoral Fellow: G. Muralidhar

Introduction

The objective of this research is to develop an insight into the basic properties of supported sulfide catalysts and to determine how these relate to coal liquids upgrading. The proposed program involves a fundamental study of the relationship between the surface-structural properties of various supported sulfide catalysts and their catalytic activities for various types of reactions. Thus, there are two clearly defined and closely related areas of investigation, viz., (1) catalyst characterization, especially of the sulfided and reaction states and (2) elucidation of the mode of interaction between catalyst surfaces and organic substrates of different types. The study of subject (1) will provide basic data on sulfided catalyst structure and functionality, and would allow the development of catalyst surface models. Subject (2), on the other hand, involves systematic studies of model reactions on sulfide catalysts, and the utilization of data obtained for development of molecular level surface reaction models correlating the geometry (and topography) of catalyst surfaces with the steric-conformational structure of adsorbed organic reactants. The overall objective of the project is to provide fundamental data needed for design of specific and more effective catalysts for upgrading of coal liquids.

Atmospheric activity tests using model compounds representative of hydrodesulfurization (thiophene), hydrogenation (hexene) and cracking (isooctene) have been developed. These were employed to assay changes in the catalytic functions of various supported CoMo catalysts. It was found that hydrodesulfurization (HDS) and hydrogenation activities were generally unaffected by the type of alumina used or by the cobalt salt used in the preparation; whereas, cracking activity varied considerably, being highest for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and cobalt sulfate addition. In a series of catalysts employing silica-alumina as the support, the two former functions decreased with increasing silica content, while cracking went through a maximum in activity. Addition of acidic, basic or neutral ions to the standard catalyst at 0.5 wt % level showed interesting changes in catalytic activities for various functions. Acidic ions like F and Cl increased catalytic activity for HDS and cracking reactions whereas the hydrogenation function was not affected. Basic additives like Na decreased hydrodesulfurization activity while hydrogenation activity did not show any appreciable change. Neutral ions like Mg and Zn did not influence any of the functions.

## Project Status

During this quarter, the effects of varying the pretreatment procedure with the standard CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and of different supports on resultant catalyst activities were investigated. All catalysts were prepared by incipient wetness impregnation and calcined at 540°C.<sup>1</sup> The composition of the active components was 3% Co and 8% Mo. Catalyst activities for hydrodesulfurization (HDS), hydrogenation and cracking were determined at 350°C in a fixed-bed, microcatalytic reactor at atmospheric pressure using thiophene, hexene-1 and isooctene, respectively. Details of experimental procedures were described earlier.<sup>2</sup>

It is well known that the sulfided form of CoMo catalysts is active for HDS. However, the reduced form also has considerable activity. Previous studies on Mo catalysts have shown that different reduction and sulfiding pretreatments can have an influence on HDS activity for thiophene.<sup>3</sup> With a view to acquiring data on the influence of pretreatment on our standard CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, various reduction and sulfiding procedures were studied. Catalyst activity data for HDS, hydrogenative and cracking are presented in terms of rate constants in Table 1. Significant differences in catalyst activities were obtained by these treatments.

The standard sulfiding pretreatment adopted for previous testing consists of treating the catalyst with 10% H<sub>2</sub>S/H<sub>2</sub> for two hours at 400°C, followed by cooling to 350°C in He (Run 1).<sup>2</sup> In Run 2, the catalyst was only oven-dried at 110°C instead of the normal 540°C calcination. It was quickly heated to 400°C in He and then immediately sulfided for two hours. The resultant catalyst showed lower HDS activity, higher cracking activity and the same hydrogenation activity as for the standard calcined catalyst (Run 1). The effects of reduction in H<sub>2</sub> at 400°C prior to sulfiding (Run 3) was minimal on HDS and hydrogenation,<sup>2</sup> but increased cracking; whereas a 500°C reduction (Run 4) resulted in lower HDS activity. It is likely that a temperature of 400°C is too low to achieve much reduction of the active components, which are in an oxide state from the catalyst calcination in air. However, at 500°C, appreciable reduction in H<sub>2</sub> can result in a lower valence state of the Mo and Co with formation of anion vacancies. Previous work on Mo/Al<sub>2</sub>O<sub>3</sub> has shown that prereduced catalysts add less sulfur during the subsequent sulfiding step.<sup>4</sup> It is believed that both anion vacancies and sulfide ions are important for HDS activity.<sup>3</sup> Therefore, a lower sulfide level in the 500°C reduced catalyst would result in a reduced number of active vacancy-sulfide ion pairs and consequent lower HDS activity. Whatever the explanation, it is interesting that prereduction did not affect hydrogenation activity and markedly increased cracking activity. This reinforces an earlier conclusion that the three reactions take place on different sites.<sup>5</sup> The lack of change in hydrogenation must certainly indicate that no appreciable change in dispersion of the active phase occurred due to reduction, since previous results had shown a lowering of both HDS and hydrogenation with catalysts having lower active phase dispersions.<sup>1</sup> If this is so, then the lower HDS activity for the prereduced catalysts would indicate a loss of localized active surface sites for HDS without benefit of appreciable structural changes in the active phase. The reason for the increase in cracking activity with prereduction is not clear at present.

In Runs 5 and 6, the catalyst was not presulfided prior to exposure to thiophene. A prereduction in this case (Run 5) gave a catalyst having the lowest HDS activity; whereas no pretreatment (Run 6) resulted in a moderate activity loss for HDS. Since thiophene has been found to be less effective

in sulfiding a Mo/Al<sub>2</sub>O<sub>3</sub> catalyst than H<sub>2</sub>S,<sup>3</sup> it may be surmised that the lower activity in these cases is due to lower sulfur content of the catalysts, as has been discussed above. Again, the hydrogenation activities were not affected by these treatments.

Table 2 presents data on the effect of various supports on catalyst activity. All gave significantly lower HDS and hydrogenation activities than for Al<sub>2</sub>O<sub>3</sub>. This is most likely due to poorer dispersion of the active phase in these catalysts, as they all showed evidence of crystalline CoMoO<sub>4</sub> in the oxide state by X-ray diffraction analysis. The higher cracking activity for the SiO<sub>2</sub>-MgO catalyst is undoubtedly due to the support itself, which is highly acidic. Similar effects were observed with SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>1</sup> The low cracking activities for the SiO<sub>2</sub> and C catalysts can be attributed to the active acid character. From the results obtained thus far, it appears that an Al<sub>2</sub>O<sub>3</sub> support is the best to achieve highest HDS and hydrogenation activity.<sup>2</sup> This can be attributed to the high degree of support-active phase interaction in the calcined catalyst, resulting in a high dispersion of the active phase,<sup>6</sup> which is maintained in the sulfided state.

### Future Work

Sulfur analyses and additional X-ray diffraction data will be obtained on the various CoMo catalysts to relate to catalyst activities. A technique to determine oxygen chemisorption on the sulfided catalysts is under investigation. A dry box to interface with the ESCA instrument so that sulfide samples can be examined without exposure to air is on order. As soon as this is available, work will start on characterization of sulfide catalysts with ESCA. Some additional CoMo catalysts on modified Al<sub>2</sub>O<sub>3</sub> supports have been prepared and will be tested. Preparation and testing<sup>3</sup> of catalysts containing Ni and W will begin.

### References

1. W. H. Wiser, F. E. Massoth, J. Shabtai and G. Muralidhar, DOE Contract No. DE-AC01-79ET14700, Quarterly Progress Report, Salt Lake City, Utah Apr-Jun, 1980.
2. *ibid.*, July-Sept, 1980.
3. C. L. Kibby and F. E. Massoth, *J. Catal.*, 47, 300 (1977).
4. F. E. Massoth, *J. Catal.*, 36, 164 (1975).
5. R. Ramachandran and F. E. Massoth, *J. Catal.*, 67, 248 (1980).
6. F. E. Massoth, *Adv. Catal.*, 27, 265 (1978).



Table 1. Effect of Pretreatment on Activity of CoMo Catalysts<sup>a</sup>

Run No.	Pretreatment <sup>b</sup> Temperature, °C		Rate Constants <sup>c</sup>		
	Reduction	Sulfiding	$k_T$ cm <sup>3</sup> /g min atm	$k_H$ cm <sup>3</sup> /g min	$k_C$ cm <sup>3</sup> /g min
1	none	400	32.8	60.9	155
2	none	400	23.8	58.7	182
3	400	400	35.8	67.9	231
4	500	400	20.2	60.1	211
5	500	none	8.0	58.3	148
6	none	none	19.2	57.4	224

<sup>a</sup>All catalysts contained 3% Co and 8% Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

<sup>b</sup>All catalysts were calcined at 540°C, except for number 2, which was only dried at 110°C.

<sup>c</sup> $k_T$  for HDS,  $k_H$  for hydrogenation,  $k_C$  for cracking.

Table 2. Support Effects on Activity of CoMo Catalysts

Support <sup>a</sup>	Rate Constants <sup>b</sup>		
	$k_T$ cm <sup>3</sup> /g min atm	$k_H$ cm <sup>3</sup> /g min	$k_C$ cm <sup>3</sup> /g min
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	32.8	60.9	155
SiO <sub>2</sub>	11.7	8.1	84
SiO <sub>2</sub> -MgO <sup>c</sup>	11.9	29.9	528
TiO <sub>2</sub>	6.9	18.5	231
C	6.0	34.0	78

<sup>a</sup>3% Co and 8% Mo.

<sup>b</sup> $k_T$  for HDS,  $k_H$  for hydrogenation,  $k_C$  for cracking.

<sup>c</sup>27% MgO-73%SiO<sub>2</sub>.

## Diffusion of Polyaromatic Compounds in Amorphous Catalysts Supports

Faculty Advisor: F.E. Massoth  
Graduate Student: A. Chantong

### Introduction

This project involves assessing diffusional resistances within amorphous-type catalysts. Of primary concern is the question of whether the larger, multiring hydro-aromatics found in coal-derived liquids will have adequate accessibility to the active sites within the pores of typical processing catalysts. When molecular dimensions approach pore size diameters, the effectiveness of a particular catalyst is reduced owing to significant mass transport resistance. An extreme case occurs when molecular and pore size are equivalent, and pores below this size are physically inaccessible.

The project objective can be achieved through a systematic study of the effect of molecular size on sorptive diffusion rates relative to pore geometry. Conceptually, the diffusion of model aromatic compounds is carried out using a stirred batch reactor. The preferential uptake of the aromatic from the aliphatic solvent is measured using a UV spectrometer. Adsorption isotherms are determined to supplement the diffusion studies.

Initial work entailed development of a suitable reactor, measurement techniques and methods of data analysis. These demonstrated that adsorption was diffusion-controlled. Effective diffusivities were larger than predicted for pore diffusion and a surface diffusion contribution was postulated. Subsequent studies were extended to other multiaromatic compounds and aluminas with similar results. The fractional surface diffusion contribution was appreciable and about the same in all cases. Because of this, restrictive diffusion effects could not be properly evaluated. However, for the largest size compound (20 Å) and smallest average pore size alumina (50 Å) tested, a markedly lower diffusivity was obtained, indicative of a restrictive diffusion effect.

### Project Status

The adsorption isotherms for catalysts L, D, C and M with solutes naphthalene, coronene and tetra-phenylporphine in cyclohexane were completed. All of the data fit a Freundlich isotherm, which is represented by the following expression,

$$Q = kc^{1/n} \quad (1)$$

where  $Q$  is the solute uptake in  $\text{mg}/\text{cm}^3$ ,  $c$  is the final solution concentration in  $\text{mg}/\text{cm}^3$  and  $k$  and  $n$  are constants. The constants  $k$  and  $n$  for all the solutes and catalysts studied are given in Table 1. As the aromaticity of the solute increases, the curvature of the isotherm (value of  $n$ ) increases.

Solute uptakes (related to  $k$ ) also increase with molecular size. Catalyst effects are less pronounced, although a decreasing trend in  $k$  and  $n$  with increasing average pore size is generally observed. The values of  $n$  are used for calculating effective diffusivities.

Effective diffusivities of the solutes in catalysts L, D, C and M were measured in diffusion experiments; the results are presented in Table 2. From the following relation of the effective diffusivity in porous solids,

$$D_e = \frac{D_b \epsilon K_r}{\tau} \quad (2)$$

where  $D_e$  is the effective diffusivity coefficient in  $\text{cm}^2/\text{sec}$ ,  $D_b$  is the bulk diffusivity coefficient in  $\text{cm}^2/\text{sec}$ ,  $\epsilon$  is porosity of the catalyst,  $\tau$  is the tortuosity of the catalyst and  $K_r$  is the restrictive coefficient,  $K_r/\tau$  for each solute-catalyst pair can be calculated.

In gas systems, where the molecular diameter of the gas is usually small compared to the pore size of the catalyst, the tortuosity of the catalyst is taken to be characteristic of the porous structure, but not the nature of the diffusing molecule.<sup>1</sup> In the system under investigation, involving a liquid phase, the molecular diameter of diffusing molecules are not small when compared to the pore size of the catalysts. Also there are big differences in molecular diameter of the diffusing molecules; for example, naphthalene with molecular diameter of 7 Å to tetraphenylporphine with molecular diameter of 19 Å. Therefore, the tortuosity can no longer be taken to be characteristic of the porous structure alone, but it is also a function of the molecular size of the diffusing molecule.<sup>2,3</sup>

Because values of  $\tau$  are not known,  $K_r$  and  $\tau$  are lumped together as one variable parameter  $K_r/\tau$ . This parameter combines both the restrictive effect and the combined effect of pore structure and molecular size. For the larger diffusing molecules, the  $\tau$  value would be larger and  $K_r$  smaller. Therefore  $K_r/\tau$  would be expected to decrease as the ratio of critical solute molecular diameter to pore diameter increases. Values of  $K_r/\tau$  from the experimental data are plotted against the ratio of critical solute molecular diameter to pore diameter ( $d_s/d_p$ ) in Figure 1.

Beck and Schultz<sup>2</sup> studied diffusion rates of several compounds with molecular diameters from 5.2 to 43 Å in mica membranes. The mica membranes were prepared with uniform, straight pores from 96 to 600 Å in diameter and 3 to 5 micrometers thick. Their results showed a large effect of ratio of solute critical diameter to pore diameter on pore diffusion rates. At a size ratio of solute to pore of 1/10, the pore diffusion rate was about 40 percent less than its bulk diffusivity.

Their results are plotted as a solid line in Figure 1. Satterfield et al.<sup>4</sup> also measured diffusion rates of both nonadsorbing solutes and preferentially adsorbed solutes in a silica-alumina bead catalyst (pore diameter 32 Å). Their data for preferentially adsorbed solutes are also plotted in Figure 1. The results from the present study agree reasonably well with results of these investigators.

The general agreement between these sets of data is somewhat surprising since quite different systems were studied. Beck and Schultz used mica

membranes (pore diameter 96-600 Å) with nonadsorbing solutes (equilibrium coefficient  $K_p \approx 1$ ), Satterfield used a silica alumina catalyst (pore diameter 32 Å) with slightly preferentially adsorbed solutes ( $K_p = 2.4-182$ ), and in the present study highly preferentially adsorbed solutes ( $K_p \approx 40-4000$ ) with gamma aluminas (pore diameter 49-154 Å) were used. Thus, it appears that the restrictive diffusion correlation of Figure 1 is a general one that may apply to all systems. However, further experimentation will be required to confirm this conclusion.

### Future Work

Satterfield and Cheng<sup>5</sup> measured diffusion rates of organic compounds in type Y zeolites. They found that not only the critical molecular diameter of the diffusing molecules affected the rate of diffusion, but also the interaction between diffusant and zeolite affected diffusion rates. Molecules with higher polarity had lower mobility in the zeolite channels as a result of this interaction. To check whether this effect is important in our system, the diffusion rate of quinoline will be measured and compared to the diffusion rate of naphthalene. Quinoline has about the same critical molecular diameter as naphthalene but has a higher polarity. If the polarity of the solute is not an important factor, the same diffusion rates should be obtained from these two compounds.

Several investigators<sup>6,7</sup> have found that the effective diffusivities of organic compounds in both zeolites and activated carbon are strongly dependent on the concentration; this was explained by the occurrence of surface diffusion. Both surface diffusion fluxes and surface diffusion coefficients were found to be strongly concentration dependent.<sup>8,9</sup> Experiments to check the concentration dependence of the effective diffusivity in our system will be carried out.

### References

1. C.N. Satterfield, "Mass Transfer in Heterogeneous Catalysis," The Colonial Press, Inc., Massachusetts, 1977, p 40.
2. R.E. Beck and J.S. Schulz, Science, 170, 1302 (1970).
3. J.S. Schultz and P. Gerhardt, Bact. Rev., 33, 1 (1969).
4. C.N. Satterfield, C.K. Colton and W.H. Pitcher, Jr., AIChE Journal, 19, 628 (1973).
5. C.N. Satterfield and C.S. Cheng, Chem. Eng. Progr., 67, 43 (1972).
6. D.M. Ruthven and I.H. Doetsch, AIChE Journal, 22, 882 (1976).
7. W. Fritz, W. Merk and E.V. Schlunden, Chem. Eng. Sci., 36, 731 (1981).
8. E.R. Gilliland, R.F. Baddour, G.P. Perkinson and K. Sladek, Ind. Eng. Chem., Fundam., 13, 95 (1974).
9. K.J. Sladek, E.R. Gilliland and R.F. Baddour, ibid., 13, 100 (1974).

Table 1. Freundlich Isotherm Constants.

Solute	Catalyst <sup>a</sup>	k <sup>b</sup>	n <sup>b</sup>
Naphthalene	L	33	1.31
	M	30	1.28
	D	27	1.26
	C	22	1.19
Coronene	L	170	1.71
	M	140	1.65
	D	128	1.57
	C	123	1.39
Tetra-Phenyl porphine	L	185	3.09
	M	150	2.98
	D	135	2.85
	C	87	3.16

<sup>a</sup>Average pore sizes,  $d_p$ , are: L-49, M-72, D-98, C-154 Å.

<sup>b</sup>Values of constants in Eq. (1).

Table 2. Effective Diffusivity Coefficients.

	$D_e \times 10^6, \text{cm}^2/\text{sec}$			
	Catalyst L $d_p = 49 \text{ Å}$	Catalyst M $d_p = 72 \text{ Å}$	Catalyst D $d_p = 98 \text{ Å}$	Catalyst C $d_p = 154 \text{ Å}$
Naphthalene $d_s = 6.9 \text{ Å}$	3.4	3.45	4.08	6.95
Coronene $d_s = 11.1 \text{ Å}$	2.11	2.365	2.82	4.14
Tetra-phenyl- porphine $d_s = 19 \text{ Å}$	0.47	0.66	1.43	1.49

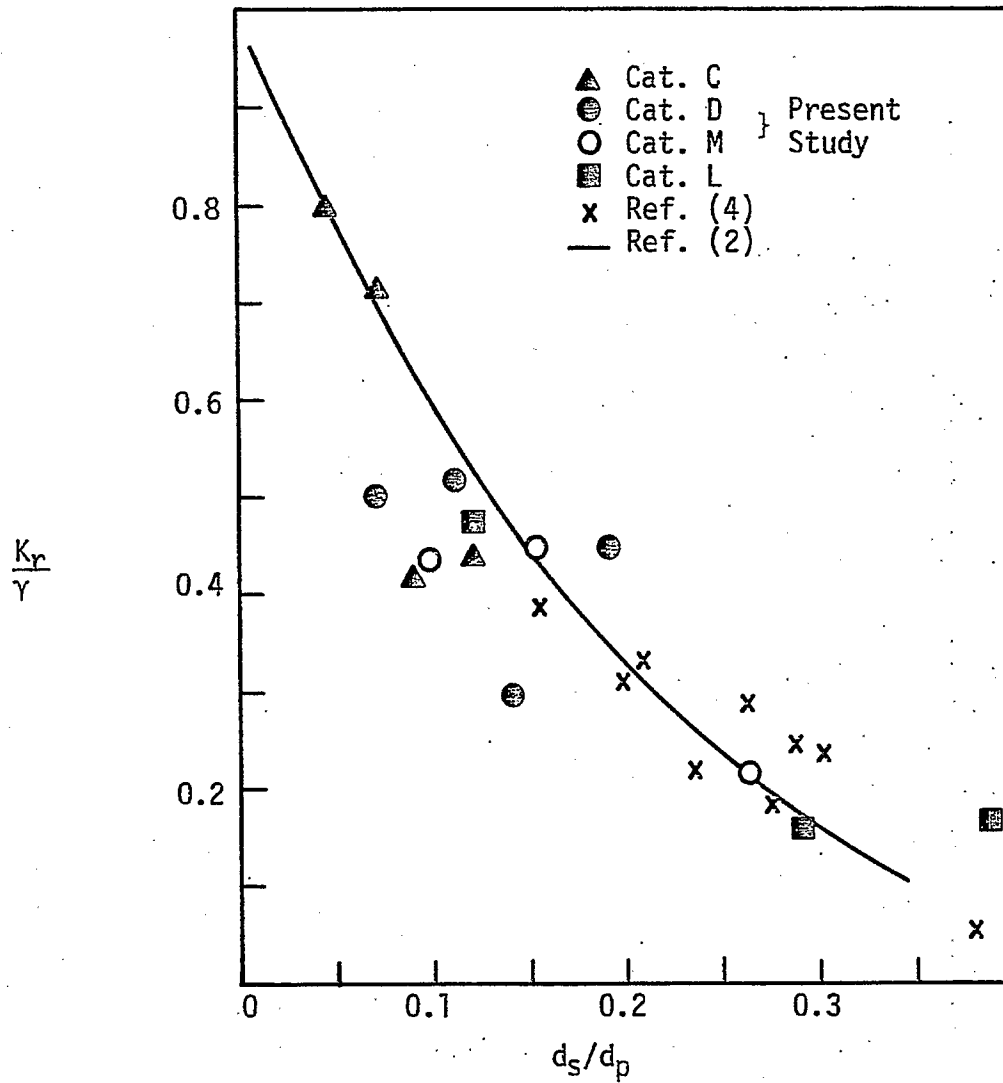


Figure 1. Effect of Ratio of Solute Critical Diameter to Pore Diameter on Effective Diffusivity.

## Task 13

### Catalyst Research and Development

Faculty Advisor: F.V. Hanson  
Graduate Student: C.S. Kim

#### Introduction

The objectives of this project are to develop a preparation technique for a Raney type catalyst (particularly Raney iron-manganese catalyst) and to find the optimum process variables for the maximum production of low molecular weight olefins and/or BTX via hydrogenation of carbon monoxide. A detailed description of the objectives are in a previous report.<sup>1</sup>

A fixed-bed reactor system was fabricated to conduct catalyst screening tests to determine the optimum process variables and to study the overall kinetics of the hydrogenation of carbon monoxide over Raney type catalyst. An electrical heating furnace was built to produce various aluminum alloys with different compositions and components.

Several samples of aluminum-iron alloys were made in the furnace and optimum heating and cooling conditions were found.

#### Project Status

Three types of aluminum alloys (Al-Fe, Al/Fe=55/45 wt %; Al-Fe-Mn, Al/Fe/Mn=60/38/2; Al-Mn, Al/Mn=40/60) were prepared in the same manner as reported in the previous report except that the hot melt was quenched by casting the melt on a stainless steel plate, whose bottom was in contact with water for fast heat dissipation. This casting step is believed to contribute some degree of mixing and thereby reduce major segregation problems.

A part of each alloy was subjected to a homogenization heat treatment. Each alloy sample was placed in a quartz tubing, evacuated, sealed and then heated in a muffle furnace. Table 1 shows the heat treatment conditions for alloy preparation and for homogenization.

The X-ray powder diffractions were done for each cast and homogenized sample of the alloys to identify the major phases present in the samples. The X-ray powder diffractions were made on a Philips Norelco vertical goniometer. The alloys were crushed into fine particles to pass through a 270 mesh sieve. Collimated copper radiation ( $\text{CuK}\alpha$ ) was diffracted from the mounted sample to a bent graphite monochromator set and then the radiation was transmitted to a scintillation counter. The tube current and voltage were 20 mA and 35 Kv, respectively. Each sample was scanned between  $20^\circ$  ( $2\theta$ ) to  $70^\circ$  ( $2\theta/\text{min}$ ).

Each cast sample showed the diffraction pattern of the corresponding phase found from the phase diagrams<sup>2</sup> as listed in Table 1. No other peaks

with noticeable intensities were found except those of the phases in Table I.

Any differences in the X-ray diffraction patterns between the cast sample and the homogenized one were not found, although the homogenized sample showed smoother background and sharper peak intensities, presumably due to the annealing effect after homogenization.

An optical microscope was used to examine the two-dimensional surface of the Al-Fe alloy. The alloy samples were mounted on an epoxy resin. This mounted specimen was ground and polished to expose an undistorted surface according to the procedures in the literature.<sup>3</sup> Grinding was done with silicon carbide abrasive papers in order of decreasing particle sizes (240, 320, 400, 600 grit). The surface was polished with magnesium oxide fine powders on a rotating wheel as suggested by Mondolfo.<sup>4</sup> This polished surface of the Al-Fe alloy was etched with 20% sulfuric acid solution for 1 min<sup>2</sup> to reveal the grain boundaries. These boundaries could be clearly seen under the optical microscope. Some black spots were found on the surface, sometimes across the grain boundaries. Since an examination of an unetched sample showed the same black spots, it was assumed that these black spots originated from porosities of the sample, not a second phase. These porosities may come from the shrinkage of the alloy during quenching and gas entrapment such as hydrogen produced by the reaction of the moisture in the air with the hot surface of the alloy melt.

A detailed identification of the phases in each type of alloy with an electron probe microanalyzer (EPMA) could not be done due to the breakdown of the instrument.

A catalyst activation and washing unit were set up to activate the alloys and to wash the remaining alkalis as shown in Figures 1 and 2.

### Future Work

The identification of the phases in the alloys will be confirmed by an EPMA. The uniformity of the alloy samples will also be examined using the above technique.

The activation of the catalyst and the activity test with a fixed-bed reactor will be initiated.

### References

1. W.H. Wiser, F.V. Hanson and C.S. Kim, DOE Contract No. DE-AC01-79ET14700, Quarterly Progress Report, Salt Lake City, Utah, Oct-Dec 1979.
2. Metal Handbook, Vol 8, 8th Ed., ASME (1973).
3. Technical Notes, Buehler Ltd.
4. L.F. Mondolfo, "Metallography of Aluminum Alloys," John Wiley & Sons, New York, 1973.



Table 1

Alloy Type	Al-Fe	Al-Fe-Mn	Al-Mn
Alloy preparation Temp/heating time	1250°C/12 hr	1250°C/12 hr	1250°C/24 hr
Homogenization Temp/heating time	500°C/1 hr 975°C/2 days	600°C/2 hr 950°C/2 days	1000°C 2 days
	500°C/1 hr 975°C/4 days	600°C/2 hr 950°C/4 days	1000°C 4 days
Phases	Fe <sub>2</sub> Al <sub>5</sub>	FeAl <sub>3</sub>	MnAl

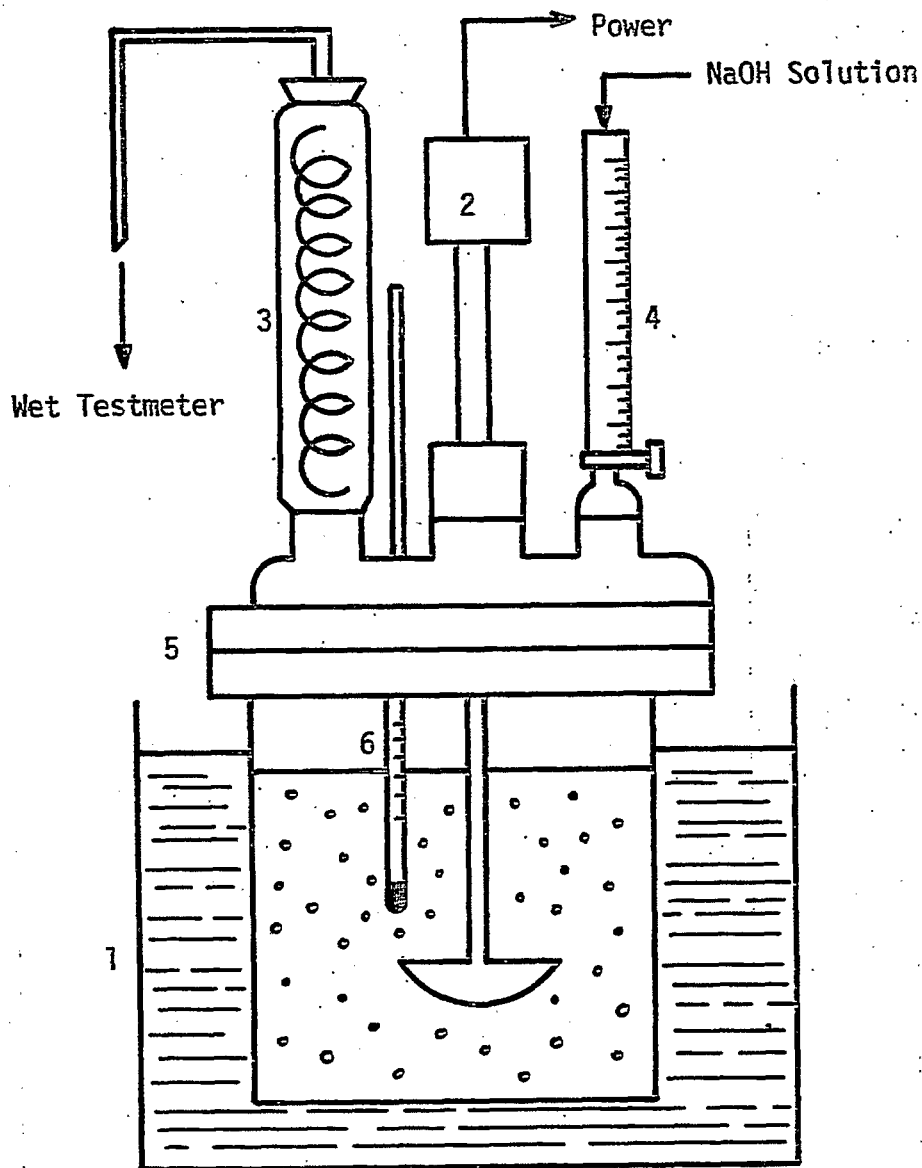


Figure 1. Catalyst Activation Apparatus.

1. Const. Temp. Water Bath
2. Stirring Motor
3. Condenser
4. Burette
5. Four-Opening Resin Flask
6. Thermometer

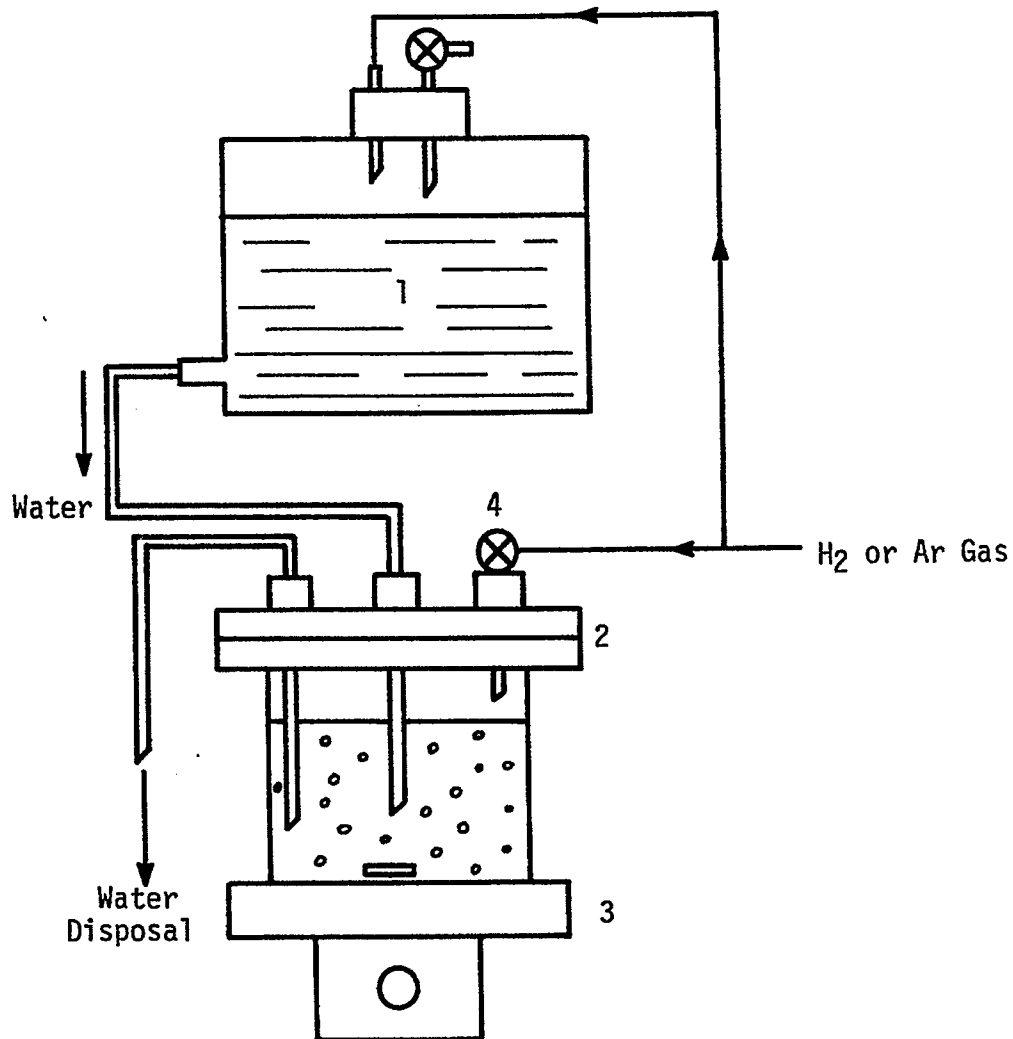


Figure 2. Washing System.

1. Washing Water Reservoir
2. Washing Flask with Four Openings
3. Magnetic Stirrer
4. Two-Way Stopcock

## Task 13

### Catalyst Research and Development

#### Synthesis of Light Hydrocarbons from CO and H<sub>2</sub>

Faculty Advisor: F.V. Hanson  
Graduate Student: Y.S. Tsai

#### Introduction

The hydrogenation of carbon monoxide to produce low molecular weight olefins (C<sub>2</sub>-C<sub>4</sub>) has been studied over a series of unsupported iron-manganese catalysts in a bench-scale fixed-bed reactor system. The results indicated that an iron-manganese catalyst composed of 2.2 parts manganese per 100 parts iron (atomic ratio) was selective for the C<sub>2</sub>-C<sub>4</sub> olefin production. Effects of process parameters on the product yield and selectivity over a subset of iron-manganese catalysts has been completed. Most of the data were in agreement with those found in the literature.

Three important steps have been considered to obtain a more comprehensive analysis of the catalyst performance. These steps include: (1) the fabrication of a new fixed-bed reactor system, (2) the establishment of the catalyst characterization procedures and (3) the effect of various catalyst pretreatments and catalyst preparation. The advantages to be derived from the steps taken above will be a more accurate material balance, the clear nature of the catalyst surface corresponding to the catalyst activity and selectivity as well as the optimal catalyst pretreatments for the maximum yield and selectivity.

#### Project Status

The preliminary design of the new fixed-bed reactor system is completed. Some important equipment has been purchased. The fabrication will be carried out as soon as all the equipment has arrived.

The procedure for catalyst characterization is being pursued. A literature survey on the hydrogenation of carbon monoxide is also being undertaken.

#### Future Work

The fabrication of the new reactor system will be carried out extensively after all the equipment is acquired. Characterization of the Fe/Mn catalysts will be conducted to determine the catalyst nature. The literature survey will also be continued to keep abreast of the latest developments for carbon monoxide hydrogenation.

## Characterization of Catalysts and Mechanistic Studies

Faculty Advisor: F.E. Massoth  
Graduate Student: K.B. Jensen

### Introduction

This phase of the project is intended to supplement the high pressure reactor studies by detailed examination of the catalyst properties which enhance catalyst activity and selectivity. This is accomplished by characterization studies performed on fresh catalysts and on the same catalysts which have been run in the reactor. Of particular interest are metal areas, phase structure, catalyst stability and surface characteristics. Also, variables in catalyst preparation and pretreatment are examined to establish their effects on catalyst properties. Finally, in-situ adsorption and activity are studied under modified reaction conditions with a number of well-characterized catalysts to obtain correlating relationships. The catalysts under present investigation are iron-based catalysts promoted with manganese oxide.

Previous work had shown the reduced catalysts have low surface areas ( $<10 \text{ m}^2/\text{g}$ ) and are composed of two principal phases,  $\alpha$  iron and manganese (II) oxide. Some used catalysts were also found to contain small amounts of possible iron oxide and iron carbide phases. Investigations using the scanning electron microscope indicated that the MnO phase is well dispersed in the catalysts and X-ray line broadening results indicated that the MnO particles or possible layers average in the order of  $200 \text{ \AA}$  in breadth. Some iron (II) oxide (FeO) is also indicated to be present in the MnO phase by X-ray diffraction.

Preliminary carburization studies gave two general regimes of carburization, an early fast carburization followed by a slower one. The presence of MnO promoter was found to slow carburization.

Temperature programmed reaction/desorption studies support the interpretation of some dissociative chemisorption of CO on the iron containing catalysts; also that a relatively strong interaction exists between the catalysts and both adsorbed carbon and oxygen. The pure MnO catalyst was found to be generally inactive toward CO but did adsorb CO<sub>2</sub> and O<sub>2</sub>.

Data from X-ray diffraction, BET surface area, and CO and O<sub>2</sub> chemisorption experiments have been used to produce tentative structural models for the low manganese and high manganese iron catalysts. The low manganese catalysts have a significant portion of their potential iron surface area covered by smaller particles of manganese oxide. The high manganese catalysts seem to be iron and MnO particles showing relatively little interaction.

## Project Status

In the Fischer-Tropsch synthesis,  $\alpha$ -olefin products have long been observed and often described as the primary products of the hydrogen-carbon monoxide reaction. These olefins are thought to participate in paraffin production via subsequent hydrogenation.<sup>1</sup> Since one of the principle characteristics of the iron based manganese catalysts is their relatively high selectivity to olefins, their hydrogenation activity was investigated. Hydrogenation of 1-hexene was chosen as the model reaction.

The procedure followed for the hexene hydrogenation experiments is similar to that used in this laboratory to test the hydrogenation activity of used H-coal catalysts.<sup>2</sup> Approximately 4 g of prereduced catalyst was loaded in the reactor and then heated to 500°C in flowing hydrogen for an hour or more to remove surface oxygen. The catalyst was then cooled to room temperature and hexene was introduced into the hydrogen gas stream using two bubbles in series, the first bubbler at room temperature and the second at 0°C. The products of reaction were analyzed using a gas chromatograph. Pseudo-first order rate constants were determined for the hydrogenation reaction. Thermodynamically, the hydrogenation reaction is essentially irreversible at the conditions employed. Two other reactions were also observed on the catalysts, double bond isomerization and hydrogenolysis. No skeletal isomerization was observed. Double bond migration occurred at lower temperature in general than hydrogenation. The hydrogenolysis reaction became significant at higher temperatures.

The freshly reduced catalysts were found to be very active toward hexene hydrogenation. The pure iron catalyst completely converted hexene to hexane at room temperature. The presence of manganese oxide did appear to lower the hydrogenation activity of the catalysts somewhat, but these catalysts were also very active. Manganese oxide itself, however, showed virtually no hydrogenation activity.

A carburization pretreatment had a substantial effect on the activity of the iron catalyst for hexene hydrogenation. Table 1 shows the calculated hydrogenation rate constants of freshly reduced iron (catalyst C-0) and iron carburized 3 hours at 250°C in a 2H<sub>2</sub>/CO mixture. The hydrogenation activity over the carburized catalyst was significantly lowered compared to the fresh catalyst. This is most likely due to a carbon overlayer on the catalyst,<sup>3</sup> either reducing the number of active iron sites or causing a diffusion limitation to the reaction by virtue of a need to diffuse the reactant through the carbon layer to reach the iron surface. Reaction of hexene in a 2H<sub>2</sub>/CO gas mixture further reduced the hydrogenation activity over the precarburized catalyst. If the hydrogenation rate is proportional to the hydrogen partial pressure, a lowering of the hydrogenation rate by 2/3 would be expected. The much greater effect is probably due to competitive adsorption of CO for the active sites, thus lowering their concentration for hexene adsorption. Of course, the synthesis gas hydrogenation conditions more closely represent those during Fischer-Tropsch synthesis and better approximate the actual hydrogenation activity of the catalyst.

Table 2 shows the hydrogenation activity in synthesis gas of several catalysts after carburization. The specific rate constant based on previously determined iron area from chemisorption measurements are also listed. The presence of manganese in the C-5 to C-39 catalysts has approximately halved the rate constant of the pure iron catalyst on a weight basis. Interestingly, on a iron surface area basis the rate constants are quite similar.

However, the high manganese catalyst (C-74) shows a higher intrinsic hydrogenation activity than pure iron. This result is consistent with the lower olefin to paraffin ratio observed for the high manganese catalysts.<sup>4</sup> The reason for this behavior has not been established. The pure manganese oxide catalyst (C-100) again showed no hydrogenation activity.

Table 2 also lists the calculated activation energies shown by the catalysts for hexene hydrogenation. They are somewhat low, perhaps indicating a diffusion limitation through the carbon layer.<sup>5</sup> The activation energy is also seen to rise somewhat with manganese oxide content.

### Future Work

Work using the transmission electron microscope will be continued. Some experiments will begin on catalyst activity toward alcohol dehydration.

### References

1. H. Storch, N. Golubic and R.B. Anderson, "The Fischer-Tropsch and Related Synthesis," J. Wiley, New York, 1951.
2. T. Cable, F.E. Massoth and M.G. Thomas, Fuel Technology, in press.
3. K.M. Sancier, W.E. Isakson and H. Wise, Amer. Chem. Soc., Div. Petro. Chem., Preprints, 23 (2), 545 (1978).
4. Y.S. Tsai, M.S. Thesis, University of Utah, Salt Lake City, Utah, 1981.
5. G.L. Ott, Ph.D. Thesis, Purdue University, West Lafayette, Indiana, 1978.

Table 1

### Hexene Hydrogenation over Fe Catalyst

<u>Catalyst Pretreatment</u>	<u>Reaction Gas</u>	$k_H, \text{cm}^3/\text{g min}$		
		<u>500C</u>	<u>150C</u>	<u>250C</u>
Reduced	H <sub>2</sub>	— Complete Conversion —		
Carubrized <sup>a</sup>	H <sub>2</sub>	0.4	30.5	73.3
Carburized <sup>a</sup>	2H <sub>2</sub> /CO	<0.1	2.1	10.7

<sup>a</sup>2H<sub>2</sub>/CO at 250°C for 3 hr.

Table 2

Hexane Hydrogenation over Fe-Mn Catalysts<sup>a</sup>

Catalyst <sup>b</sup>	Fe area m <sup>2</sup> /g	k <sub>H</sub> , cm <sup>3</sup> /g min (k <sub>H</sub> <sup>0</sup> , cm <sup>3</sup> /m <sup>2</sup> min)		E <sub>a</sub> kcal/mole	
		150°C	200°C		250°C
C-0	5.5	2.08 (0.38)	6.22 (1.1)	10.7 (1.9)	9
C-5	3.1	0.72 (0.23)	3.12 (1.0)	5.7 (1.8)	12
C-39	--	0.57	3.3	6.4	14
C-74	2.1	2.53 (1.2)	17.4 (8.3)	38.6 (18.4)	15
C-100	0	<0.1	<0.1	<0.1	--

<sup>a</sup>Catalysts carburized in 2H<sub>2</sub>/CO at 250°C for 3 hours prior to run.  
Reaction gas 2H<sub>2</sub>/CO.

<sup>b</sup>Numbers signify approximate mole % Mn.



#### IV. Conclusions

Detailed conclusions are included in the reports for each task. Task 4 is no longer funded and has been discontinued. Task 11 has not been initiated as yet. No report was submitted for Task 2. No work was done under Task 15.